PB85-105880

# Environmental Characterization of Disposal of Waste Oils by Combustion in Small Commercial Boilers

GCA Corp., Bedford, MA

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Sep 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-105880

EPA-600/2-84-150
September 1984

# ENVIRONMENTAL CHARACTERIZATION OF DISPOSAL OF WASTE OILS BY COMBUSTION IN SMALL COMMERCIAL BOILERS

Prepared by

Paul F. Fennelly
Mark McCabe
Joanna M. Hall
Mary F. Kozik
Marilyn P. Hoyt
Gary T. Hunt

GCA CORPORATION
GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts

Contract No. 68-02-3168
Task Nos. 68 and 88

EPA Project Manager

Michael Petruska
Office of Solid Waste
Washington, D.C.

EPA Project Manager

Harry Freeman
Industrial Environmental
Research Laboratory
Cincinnati, Ohio

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

**TECHNICAL REPORT DATA**

*(Please read Instructions on the reverse before completing)*

| | | |
|---|---|---|
| 1. REPORT NO.<br>EPA-600/2-84-150 | 2. | 3. RECIPIENT'S ACCESSION NO.<br>PB85 105880 |
| 4. TITLE AND SUBTITLE<br>Environmental Characterization of Disposal of Waste Oils by Combustion in Small Commercial Boilers | | 5. REPORT DATE<br>September 1984 |
| | | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S)<br>Paul F. Fennelly, Mark McCabe, Joanna M. Hall, Mary F. Kozik, Marilyn P. Hoyt, Gary T. Hunt | | 8. PERFORMING ORGANIZATION REPORT NO.<br>GCA-TR-83-72-G |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>GCA Corporation<br>GCA/Technology Division<br>213 Burlington Road<br>Bedford, MA 01730 | | 10. PROGRAM ELEMENT NO. |
| | | 11. CONTRACT/GRANT NO.<br>Contract 68-02-3168<br>Task No. 68 and 88 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Industrial Environmental Research Laboratory<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Cincinnati, OH 45268 | | 13. TYPE OF REPORT AND PERIOD COVERED |
| | | 14. SPONSORING AGENCY CODE<br>EPA/600-12 |

15. SUPPLEMENTARY NOTES

10 to the 6th power

16. ABSTRACT

In this project, air emission tests were conducted on seven boilers in the size range 0.4 to 15 x $10^6$ Btu/hr while these boilers were firing waste oil. The main purpose of the project was to document the extent to which chemical contaminants in waste oil are destroyed during the combustion process. These data are of interest because one of the more common and widespread practices for disposing of waste oils is burning as a supplemental fuel.

Chemicals which were spiked into the waste oil before combustion included: chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, trichlorobenzene, 1-chloronaphthalene, 2,4,5-trichlorophenol, chlorotoluene. Destruction efficiencies ranged from 99.4 to 99.99 percent. Concentrations of these chlorinated hydrocarbons in the flue gas ranged from 40 to 400 μg/$m^3$. The concentrations of lead and zinc in the flue gas ranged between 5,000 and 72,000 μg/$m^3$ and 3,000 and 34,000 μg/$m^3$, respectively. The average emission rate of HCl from the seven boilers was 2.6 lb/hr.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT<br>Release to Public | 19. SECURITY CLASS *(This Report)*<br>Unclassified | 21. NO. OF PAGES<br>177 |
| | 20. SECURITY CLASS *(This page)*<br>Unclassified | 22. PRICE |

EPA Form 2220-1 (9-73)

## NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

CONTENTS

Figures . . . . iv
Tables . . . . v
Acknowledgments . . . . ix

1. Introduction . . . . 1
   References . . . . 4
2. Discussion of Test Results . . . . 6
   Inorganic components . . . . 8
   Organic components . . . . 14
   Conclusions . . . . 22
   References . . . . 27
3. Selection of Test Boilers . . . . 28
   Oil-fired commercial/industrial boiler population . . . . 28
   Major classifications of boiler design . . . . 28
   Boiler operating conditions . . . . 30
   References . . . . 36
4. Field Activities . . . . 37
   Oil feed system . . . . 39
   Oil sampling . . . . 39
   Flue gas sampling . . . . 41
   References . . . . 46
5. Analytical Protocols . . . . 47
   Introduction . . . . 47
   Sample bank/chain of custody procedures . . . . 47
   Fuel feed analysis . . . . 48
   Flue gas . . . . 54
   Fly ash . . . . 68
   References . . . . 73
6. Quality Assurance . . . . 75
   Introduction . . . . 75
   Sampling and field measurements quality control . . . . 75
   Laboratory analysis quality control . . . . 76
   Performance and system audits . . . . 110
   Quality problems and corrective actions . . . . 115

Appendices

A. Site Data Summaries . . . . 116
B. Sample Calculations . . . . 153
C. Calibrations . . . . 160

# FIGURES

Number | Page
1 Particle size distribution Site A . . . . . . . . . . . . . . . . . . 10

2 Particle size distribution Site D . . . . . . . . . . . . . . . . . . 11

3 Particle size distribution Site E . . . . . . . . . . . . . . . . . . 12

4 Particle size distribution Site G . . . . . . . . . . . . . . . . . . 13

5 Gas flow in Scotch boiler types . . . . . . . . . . . . . . . . . . 31

6 Characteristic emissions of residential oil burners during one complete cycle . . . . . . . . . . . . . . . . . . . . . . . 33

7 Air atomization nozzle . . . . . . . . . . . . . . . . . . . . . 35

8 Fuel feed system . . . . . . . . . . . . . . . . . . . . . . . . 40

9 Modified Method 5 train . . . . . . . . . . . . . . . . . . . . . 42

10 Integrated gas sampling train . . . . . . . . . . . . . . . . . . 44

11 Schematic of volatile organic sampling train . . . . . . . . . . . 45

12 Total ion chromatogram of fly ash extract cleaned by alumina chromatography . . . . . . . . . . . . . . . . . . . . . 70

13 Molecular ion isotope cluster for pentachlorodibenzo-p-dioxin in standard mixture . . . . . . . . . . . . . . . . . . . . . . 71

14 Molecular ion isotope cluster for pentachlorodibenzofuran in fly ash sample . . . . . . . . . . . . . . . . . . . . . . . 71

# TABLES

| Number | | Page |
|---|---|---|
| 1 | Average Atmospheric Emissions . . . . . . . . . . . . . . . . . . . | 7 |
| 2 | Combustion Characteristics . . . . . . . . . . . . . . . . . . . | 8 |
| 3 | Flue Gas Concentrations of Heavy Metals . . . . . . . . . . . . . | 9 |
| 4a | Inorganic Analysis of Firetube Flyash Samples - Site D . . . . . | 15 |
| 4b | EP Toxicity Tests on Firetube Flyash Samples . . . . . . . . . . | 15 |
| 5 | Destruction and Removal Efficiencies . . . . . . . . . . . . . . | 16 |
| 6 | Average Flue Gas Concentrations of the Volatile and Semivolatile Spike Components . . . . . . . . . . . . . . . . . . . . . . | 18 |
| 7 | Destruction and Removal Efficiencies for the Semivolatiles Spike Compounds . . . . . . . . . . . . . . . . . . . . . . . . . | 20 |
| 8 | Average Concentrations in Stack Gas of Dibenzofuran and Dioxin Species from Tests Exhibiting Detectable Levels . . . . . . . . | 21 |
| 9 | Semivolatile Analysis of Firetube Ash, Site D . . . . . . . . . . | 23 |
| 10 | Analysis for Chlorinated Dibenzofurans and Dibenzodioxins, Site D - Fly Ash . . . . . . . . . . . . . . . . . . . . . . | 24 |
| 11 | Dioxin and Dibenzofuran Content of Waste Oil Basestock and "Spiked" Waste Oil . . . . . . . . . . . . . . . . . . . . . . . . | 25 |
| 12 | Oil-Fired Commercial/Industrial Boiler Characteristics . . . . . | 29 |
| 13 | Boiler Descriptions . . . . . . . . . . . . . . . . . . . . . . | 32 |
| 14 | Required Fuel Viscosity for Various Atomization Methods . . . . . | 34 |
| 15 | Characterization of the Basestock Oil . . . . . . . . . . . . . . | 37 |
| 16 | EPA Hierarchy of Waste Incinerability . . . . . . . . . . . . . . | 38 |

TABLES (continued)

Number | Page

17 GC/MS Conditions for Volatile Organics Analyses . . . . . . . . . . 49

18 GC/ECD Conditions for Semivolatile Organic Analysis of Fuel Feed . . . . . . . . . . . . . . . . . . . . . . . . . . 51

19 Instrument Operating Parameters for IC Analysis . . . . . . . . . . 53

20 Analyses for Physical Characterizations of Oils . . . . . . . . . . 53

21 GC/ECD Conditions for Tedlar Bag Analysis . . . . . . . . . . . . 55

22 Thermal Desorption GC/MS--Instrument Operating Conditions . . . . 57

23 GC/MS Instrument Operating Conditions for VOST Analysis . . . . . 59

24 GC/MS Operating Conditions for Semivolatile Comprehensive Analysis . . . . . . . . . . . . . . . . . . . . . . . . . 62

25 Summary Listing of Dibenzofuran and Dibenzo-p-dioxin Reference Material . . . . . . . . . . . . . . . . . . . . . . . . . 64

26 GC/MS Operating Conditions for Selected Ion Monitoring . . . . . 65

27 GC/MS SIM Analysis for Dibenzofurans and Dibenzo-p-dioxins - Component Identification Criteria . . . . . . . . . . . . . . . 66

28 Quality Control Results - Analysis of Oil Samples for Volatile Organics - Concentration . . . . . . . . . . . . . . . . . . 79

29 Quality Control Data--Analysis of Volatile Organics in Triplicate Aliquots of GCA No. 29466 . . . . . . . . . . . . . . 80

30 Quality Control Results--GC/ECD Analysis of Semivolatiles in Waste Oil . . . . . . . . . . . . . . . . . . . . . . . . . 81

31 Quality Control Results--GC/ECD Analysis of Trichlorophenol in Waste Oil . . . . . . . . . . . . . . . . . . . . . . . . . 82

32 Quality Control Results--GC/ECD Analysis of Semivolatiles in Duplicate Waste Oil Aliquots . . . . . . . . . . . . . . . . . 83

33 Analysis of NBS Standard Reference Material 1634a . . . . . . . . 84

34 Quality Control Results--Analysis of NBS SRM 1085 . . . . . . . . 85

## TABLES (continued)

Number | Page

35 Quality Control Data--Analysis of Metals in Triplicate Aliquots of GCA No. 28977 . . . . . . . . . . . . . . . . . . . . . . 86

36 Quality Control Data--Analysis of Metals in Triplicate Aliquots of GCA No. 28802 . . . . . . . . . . . . . . . . . . . . . . 87

37 Analysis of NBS Standard Reference Material 1619 . . . . . . . . . 89

38 Analysis of Spiked Mineral Oil for Chlorine . . . . . . . . . . . . 90

39 Analysis of Chlorine and Sulfur in Duplicate Waste Oil Aliquots . 91

40 Quality Control Results--Permeation Tube Standards Check by GC/ECD . . . . . . . . . . . . . . . . . . . . . . . . . . 92

41 Comparison of GC/MS and GC/ECD Results for Permeation Tube Standards . . . . . . . . . . . . . . . . . . . . . . . . . . 93

42 Quality Control Results--Tenax Analysis . . . . . . . . . . . . . 94

43 Analysis of Tenax Cartridges Fortified at EMSL/RTP . . . . . . . 95

44 Quality Control Results--Method 5 Train Surrogate Recoveries . . 97

45 Quality Control Results--Method 5 Train Spikes . . . . . . . . . 99

46 Quality Control Results--GC/MS Analysis of Method 5 Train Extracts for Dibenzofurans and Dibenzodioxins . . . . . . . . . . 100

47 Quality Control Results--Analysis of NBS SRM 1649, Urban Dust--Organics . . . . . . . . . . . . . . . . . . . . . . . . . . 101

48 Quality Control Results--Analysis of NBS SRM 1648, Urban Particulate . . . . . . . . . . . . . . . . . . . . . . . . . . 102

49 Quality Control Results--Laboratory Control Sample for Analysis of Metals on Method 5 Filters . . . . . . . . . . . . . . . . . . 103

50 Quality Control Results--Analysis of NBS SRM 1633, Coal Fly Ash, for Trace Metals . . . . . . . . . . . . . . . . . . . . . . 104

51 Quality Control Results--Analysis of EPA Minerals QC Sample for Chloride . . . . . . . . . . . . . . . . . . . . . . . . . 105

52 Quality Control Results--Chloride in Impinger Solutions: Analysis of Blind QC Samples . . . . . . . . . . . . . . . . . . 106

TABLES (continued)

Number Page

53 Quality Control Results--Replicate Analysis of GCA No. 31310, Fly Ash, Site D . . . . . . . . . . . . . . . . . . . . . . . . 107

54 Quality Control Results--GC/MS Analysis of Fly Ash Samples: Surrogate Recoveries, Site D . . . . . . . . . . . . . . . . . . 108

55 Quality Control Results--Replicate Analysis of GCA No. 31310, Fly Ash, Site D, for Trace Elements . . . . . . . . . . . . . . . 109

56 Internal QC Samples Serving as Performance Audits . . . . . . . . 112

# ACKNOWLEDGMENTS

This project was completed through combined efforts of a large number of people on GCA's technical staff. Contributing to the experimental planning and project structure were Mr. Norman Surprenant and Mr. Robert Hall. The field operations were carried out under the supervision of Mr. Mark McCabe; members of the Field Crews included: Mr. Richard Graziano, Mr. Jamie Laurin and Mr. Albert Wilder.

The program required extensive work in developing and refining procedures for analyzing the complex chemical mixtures found in waste oil. Members from the Laboratory Analysis Department deserving special mention include: Ms. Coreen Kropiwnicki, Mr. Michael Thomas and Ms. Sandra Sandberg.

Quality Assurance support was provided by Ms. RoseMary Ellersick, Ms. Mary Kozik and Mr. Michael White.

## SECTION 1

## INTRODUCTION

The term "used oil" refers to automotive lubricating (crankcase) oils and industrial lubricating oils which have gone through their prescribed use cycle and as a consequence, must be disposed of or treated and reused.

Automotive and industrial lubricating oils contain additive packages which may comprise 15 percent or more of the oil by volume.[2] The additives, which augment the natural physical and chemical properties of the oil basestock may include nitrogen-containing dispersants, metal-containing detergents, rust and corrosion inhibitors, anti-wear additives, and oxidation inhibitors. Generally, these additives contain highly polar and functionalized molecules which significantly increase the performance and life of oil and equipment. Chemical compounds containing elements such as barium, calcium, magnesium, zinc, sodium, sulfur, nitrogen and phosphorous which are often found in used oils come primarily from the additive package.

During use, the constituents present in lubricating oils can undergo physical and chemical changes and the oil itself becomes contaminated from both internal and external sources. These contaminants cover a variety of chemicals, several classes of which are potentially hazardous to human health or environmental quality.

In recent years the environmental impact of the disposal of used oils has been an area of growing concern. Numerous studies conducted by State and Federal agencies have documented the presence of contaminants such as polynuclear aromatics (PNAs), chlorinated hydrocarbons and trace metals in samples of used motor oils.[1-12] Some of these compounds are present in the refined petroleum products while others are introduced during use or blended with the used oil during storage. The potential for the presence of these types of contaminants has been, in part, the reason for the recommendation for the listing of used oils as hazardous waste materials by the U.S. Environmental Protection Agency.[2,5] In addition to the potential chemical contaminants in used oil, it must also be pointed out that crude oil itself and many of the products that result from the refining of crude oil contain thousands of chemical compounds, many of which are polynuclear and polycyclic aromatic hydrocarbons.

The quantity of used oil generated in the United States has been estimated to be 1.1 x $10^9$ gallons per year. Approximately 40 percent of this amount is currently burned as a fuel to produce heat or process steam.[12]

The disposal of waste materials by combustion in boilers is of particular interest due to the large boiler population and the general lack of any specific waste oil combustion regulations. Current regulations, developed in accord with the Resource Conservation and Recovery Act (RCRA), specifically exempt facilities that combust wastes in energy producing operations from complying with the same requirements for chemical waste incinerators. In this regard, these facilities are not required to monitor integral combustion parameters such as waste feed rate, combustion temperature and carbon monoxide concentration in the exhaust gas; nor must they demonstrate the capability of the boiler to destroy selected organic components of a specific waste mixture.[13]

Boilers in the size range of 0.4 to 25 x $10^6$ Btu/hr, commonly classified as commercial sources, comprise approximately 70 percent of the commercial/industrial boiler population in the United States[14] and are of particular interest with regard to waste disposal. Because these units generally would use untreated or poorly characterized waste fuels and could be expected to provide less efficient combustion. The generally intermittent mode of operation of these boilers and the proximity of their low stack emissions to human receptors are additional causes of concern.

This test project was conducted for the Office of Solid Waste (OSW) and the Industrial Environmental Research Laboratory in Cincinnati (IERL-CI) and was designed to characterize the organic and inorganic emissions from six boilers, sized from 0.4 to 25 x $10^6$ Btu/hr, firing waste oil. The units selected for testing represent a cross section of firing techniques and heat transfer design typically found in boilers of this size range.

The test program consisted of obtaining a 4,000 gallon supply of used oil "basestock" from a licensed vendor. This "basestock" was thoroughly analyzed to document its chemical and physical properties. At the six test sites, this basestock used oil was spiked with the following compounds:

- Volatile Compounds
    - chloroform
    - trichloroethylene
    - 1,1,1-trichloroethane
    - tetrachloroethylene
- Semivolatile Compounds
    - trichlorobenzene
    - 1-chloronaphthalene
    - 2,4,5-trichlorophenol
    - chlorotoluene

Spiking levels ranged from 3,000 to 5,000 ppm for each compound. In one test, spiking levels for three of the compounds were set as high as 10,000 ppm. The specific spiking compounds used for each of the sites are identified in the individual site reports presented in Appendix A. The spiked oil was fed directly into the respective boilers; "as-fired" oil samples were then collected as close to the burner nozzle as possible while samples of combustion products were collected from the stack gas using sophisticated and ultra-sensitive gas sampling and analysis procedures. The primary purpose of the tests was to determine the destruction efficiency for the spiked contaminants in the oil. The combustion gas was also analyzed for selected products of incomplete combustion of the spiked compounds, including chlorinated dibenzofuran compounds and chlorinated dibenzodioxin compounds.

In addition to tests for measuring the destruction efficiency of the organic contaminants, tests were also conducted on emissions of metal contaminants in the used oil. Most of the metal emissions were contained in particulate matter and particle size measurements were conducted at several test sites to determine metal concentration as a function of particle size.

## REFERENCES

1. Cotton, F. O., M. L. Whisman, J. W. Goetzinger, and J. W. Reynolds. Analysis of 30 Used Motor Oils. Hydrocarbon Processing, 56(9):131-140, September 1977.

2. Mascetti, G. J. and H. M. White. Utilization of Used Oil. Aerospace Report No. ATR-78(7384)-1. Prepared for Division of Industrial Energy Conservation, U.S. Department of Energy, Washington, DC, August 1978.

3. Brinkman, D. W., M. L. Whisman, N. J. Weinstein, and H. R. Emmerson. Environmental, Resource Conservation, and Economic Aspects of Used Oil Recycling. DOE/BETC/RI-80/11, U.S. Deprtment of Energy, Bartlesville, OK, April 1981.

4. Weinstein, K. D., T. D. Myers, and S. R. Craft. Enhanced Utilization of Used Lubricating Oil Recycling Process By-Products. DOE/BC/10054-19, U.S. Department of Energy, Bartlesville, OK, March 1982.

5. U.S. Environmental Protection Agency. Report to Congress, Listing of Waste Oils as a Hazardous Waste Pursuant to Section 8(2), Public Law 96-463. EPA SW-909, Washington, DC, January 1981.

6. Becon Systems and ETA Engineering. Used Oil Burned as a Fuel. EPA SW-892, U.S. Environmental Protection Agency, Washington, DC, 1980.

7. Becker, D. A. and J. J. Comeford. Recycled Oil Program: Phase I - Test Procedures for Recycled Oil Used as a Burner Fuel. NBS Technica Note 1130, National Bureau of Standards, Washington, DC, August 1980.

8. Coyle, T. D. and A. R. Siedle. Metals in Oil: Occurrence and Significance for Reuse of Spent Automotive Lubricating Oils. In: Appendix I of NBS Special Publication 556, Measurements and Standards for Recycled Oil II, National Bureau of Standards, Gaithersburg, MD, September 1979.

9. Nims, J., R. Mayo, L. Boston, E. Logue, J. Krueger, and H. Aho. An Analysis of Waste Oil in Maine. State of Main Department of Environmental Protection, Augusta, Maine, 1981.

10. Purves, J. R. Personal Listing of Analyses of Waste Oil Provided to GCA. New Jersey Department of Environmental Protection, Trenton, NJ, November 1982.

11. Carter, R. C. Waste Lubricating Oil Characteristics - Do They Vary Geographically, Seasonally, and with Origin. In: Proceedings of the International Conference on Waste Oil Recovery and Reuse, Association of Petroleum Re-refiners, Washington, DC, February 1974.

12. Surprenant, N. F., W. H. Battye, P. F. Fennelly. The Fate of Hazardous and Non-Hazardous Waste in Used Oil Disposal and Recycling, U.S. Department of Energy, Report No. DOE/BC/10375-6, prepared by GCA Corporation, Bedford, MA, October 1983.

13. Impacts of Burning Hazardous Waste in Boilers. Prepared by Fred C. Hart Associates for SCA Chemical Services, Inc., Boston, MA. August 1982.

14. Devitt, T., et al. Population and Characteristics of Industrial/ Commercial Boilers in the United States. EPA-600/17-79-178a. August 1979.

# SECTION 2

# DISCUSSION OF TEST RESULTS

In general, the data obtained in the program indicate that the atmospheric emissions of the principal inorganic components--lead and HCl, are quantitatively more significant than the organic emissions from the six boilers tested. The average emissions of particulate, lead, HCl and the organic species of interest from each of the sources are presented in Table 1. The emissions for the organic components correspond to a range of destruction and removal efficiencies of 99.4 to 99.96 percent. Facility descriptions, summaries of the flue gas characteristics, results of the waste fuel and flue gas analyses and calculated destruction and removal efficiencies for each of the sites are presented in the site data summaries located in Appendix A.

A summary of several of the pertinent combustion gas characteristics are presented in Table 2. The average particulate emissions for the six sites has been calculated to be 0.34 lb/$10^6$ Btu. The particulate emission rate covered a range of 0.17 to 0.41 lb/$10^6$ Btu. With the exception of the smallest boiler (0.5 x $10^6$ btu/lb), which had an emission rate of 0.18 lb/$10^6$ Btu*, the particulate emission rate was relatively insensitive to size and oil atomization/firing method. This value is significantly greater than the particulate emission factors of 0.09 lb/$10^6$ Btu presented in the literature for commercial boilers firing residual oil[1] and is consistent with the measured ash content of waste oils, which is about a factory of 3 higher than that of residual oil.

The particulates emitted from these boilers typically contained 14 percent lead, 7 percent zinc, and 1 percent chlorine. The particle size measurements conducted at four of the sites, A, D, E and G indicate that the mean diameters ($D_{50}$) of the particulate samples range from 0.2 to 2 µm. The smaller $D_{50}$ values, 0.2 and 0.3 µm, were obtained from boilers using air for atomization of the fuel.

The carbon monoxide levels measured were generally less than 50 ppm. The exceptions were sites A and D where average levels of 220 ppm and 350 ppm were encountered. These boilers are equipped with burner assemblies specifically designed for No. 2 and No. 4 fuel oils. The basic design differences may, in part, account for the increased values encountered at these sites.

---

*Waste oil could not be fired effectively in the smallest unit; the basestock had to be diluted with No. 2 fuel oil in order to be properly atomized. The lower emission rate reflects this dilution with No. 2 oil having a much lower ash content.

TABLE 1. AVERAGE ATMOSPHERIC EMISSIONS (gram/hr)

| Site[b] | A[a] | C | D[a] | E | F | G |
|---|---|---|---|---|---|---|
| Particulate | 32 | 544 | 277 | 312 | 367 | 508 |
| Inorganic Components | | | | | | |
| HCl | 150 | 550 | 337 | 1050 | 600 | 1510 |
| Lead | 3.7 | 112 | 9.8 | 48 | 69 | 85 |
| Zinc | 2.0 | 52 | 5.7 | 29 | 37 | 45 |
| Organic Components | | | | | | |
| Volatile | | | | | | |
| Chloroform | 0.04 | 0.2 | 0.06 | 0.07 | 0.13 | 0.1 |
| Trichloroethane | 0.03 | 0.1 | 0.03 | 1.2 | 0.6 | 0.2 |
| Trichloroethylene | 0.06 | 0.1 | 0.10 | 0.1 | 0.05 | 0.3 |
| Tetrachloroethylene | 0.06 | 0.3 | 0.3 | 0.5 | 0.3 | 0.1 |
| Semivolatile | | | | | | |
| Trichlorobenzene | 0.02 | 0.03 | 0.10 | 0.13 | 0.07 | 0.2 |
| 1-chloronaphthalene | 0.01 | 0.02 | 0.03 | 0.05 | 0.06 | 0.2 |
| Trichlorophenol | 0.003 | 0.01 | NA | 0.04 | 0.01 | NA |
| Chlorotoluene | NA | NA | 0.02 | NA | NA | 0.3 |

[a] Waste oil diluted 50:50 with No. 2 oil to improve combustion for test purposes.

[b] Waste oil feed rates used throughout the program generally ranged from 3-30 gal/hr, depending on the size of the facility.

NA - Not analyzed, compound not spiked into fuel.

## INORGANIC COMPONENTS

Hydrogen chloride (HCl) and lead (which was concentrated primarily in particulate matter) were determined to be the principle inorganic components of the stack emissions. The average HCl emission rate for the six boilers tested was 2.6 lb/hr. (As a point of reference, this value is well below the 4.0 lb/hr emissions standard established for hazardous waste incinerators, wherein more highly concentrated chemical waste materials are destroyed).

TABLE 2. COMBUSTION CHARACTERISTICS

| | Particulate emissions | | | |
|---|---|---|---|---|
| | lb/hr | $lb/10^6$ Btu heat input | Excess air (percent) | Combustion efficiency[a] (percent) |
| A | 0.07 | 0.17 | 78 | 99.69 |
| C | 1.20 | 0.41 | 84 | 99.93 |
| D | 0.61 | 0.38 | 129 | 99.36 |
| E | 0.61 | 0.39 | 234 | 99.03 |
| F | 0.81 | 0.28 | 106 | 99.98 |
| G | 1.1 | 0.39 | 47 | 99.94 |

[a]

$$\text{Combustion efficiency} = \frac{(CO_2)}{(CO_2 + CO)} \times 100$$

The samples of flue gas particulate collected at the sites were analyzed for a total of 27 metals; only lead and zinc were consistently present at concentrations high enough to be of environmental significance.

The lead concentrations in the flue gas samples ranged from 5,380 $\mu g/m^3$ to 72,400 $\mu g/m^3$ over the six sites. Zinc concentrations were consistently about one-half the lead concentrations ranging from about 3,000 to 33,000 $\mu g/m^3$. The ratio of these concentrations was directly proportional to the concentrations of metals in the waste oil.

A dispersion model[1] was used to estimate the maximum short term ambient lead concentration downwind from a typical site. For the purpose of these calculations, a typical site was assumed to have the following characteristics:

| | |
|---|---|
| Lead emission rate* | 0.92 g/sec |
| Physical stack height | 15 m |
| Stack gas temperature | 435°K |
| Ambient air temperature | 293°K |
| Volumetric air flow | 0.5 m/sec |

Although the model has significant limitations (steady state atmospheric conditions and level terrain),[2] it indicates that during the peak heating season the primary ambient air lead standard, 1.5 $\mu g/m^3$ per calendar quarter, could be exceeded for a distance of a kilometer downwind of the site.

**Figures 1-4 show the measured cumulative percent of particle mass less** than a given diameter. In all cases, 80 percent of the particle mass in less than 10.0 µm (microns), which is one of the size cutoffs EPA is consideraing to designate inhalable particulates. In addition, the graphs also show that 80-90 percent of the lead contained in particulates exiting from the stack is contained in particles less than 2 µm in diameter. This diameter is generally considered to be the cutoff for "respirable" particles, i.e. those particles that when inhaled are captured or lodged deep within the lung. The measured particle size distributions are presented in Figures 1 through 4.

The air emissions of several additional metals, Zn, Cd, Cr, and As, were also noteworthy either on the basis of the concentration in the fuel or because of their listings as a hazardous waste consitituent in Appendix VIII.

TABLE 3. FLUE GAS CONCENTRATIONS OF HEAVY METALS ($\mu g/m^3$)

| Site | A | C | D | E | F | G | Avg. |
|---|---|---|---|---|---|---|---|
| Arsenic | 11.2 | 655 | 26.1 | 106 | 251 | 286 | 222 |
| Cadmium | 31.2 | 102 | 8.3 | 182 | 350 | 81 | 125 |
| Chromium | 62.2 | 166 | 112 | 230 | 205 | 263 | 173 |
| Zinc | 5,150 | 33,700 | 3,134 | 12,100 | 26,800 | 27,000 | 18,000 |
| Lead | 9,680 | 72,400 | 5,390 | 20,300 | 49,800 | 51,000 | 34,800 |

Mass flow calculations indicate that 40 to 50 percent of the lead and approximately 40 percent of the chloride introduced into the boilers is unaccounted for in the flue gas streams. It is generally assumed that the significant amounts of these compounds are contained in the fly ash deposited in the firetube sections of the boilers.

---

*As an example, this would correspond to a 2 x $10^6$ BTU/hr boiler burning uncut waste oil with a Pb concentration of 1,500 ppm.

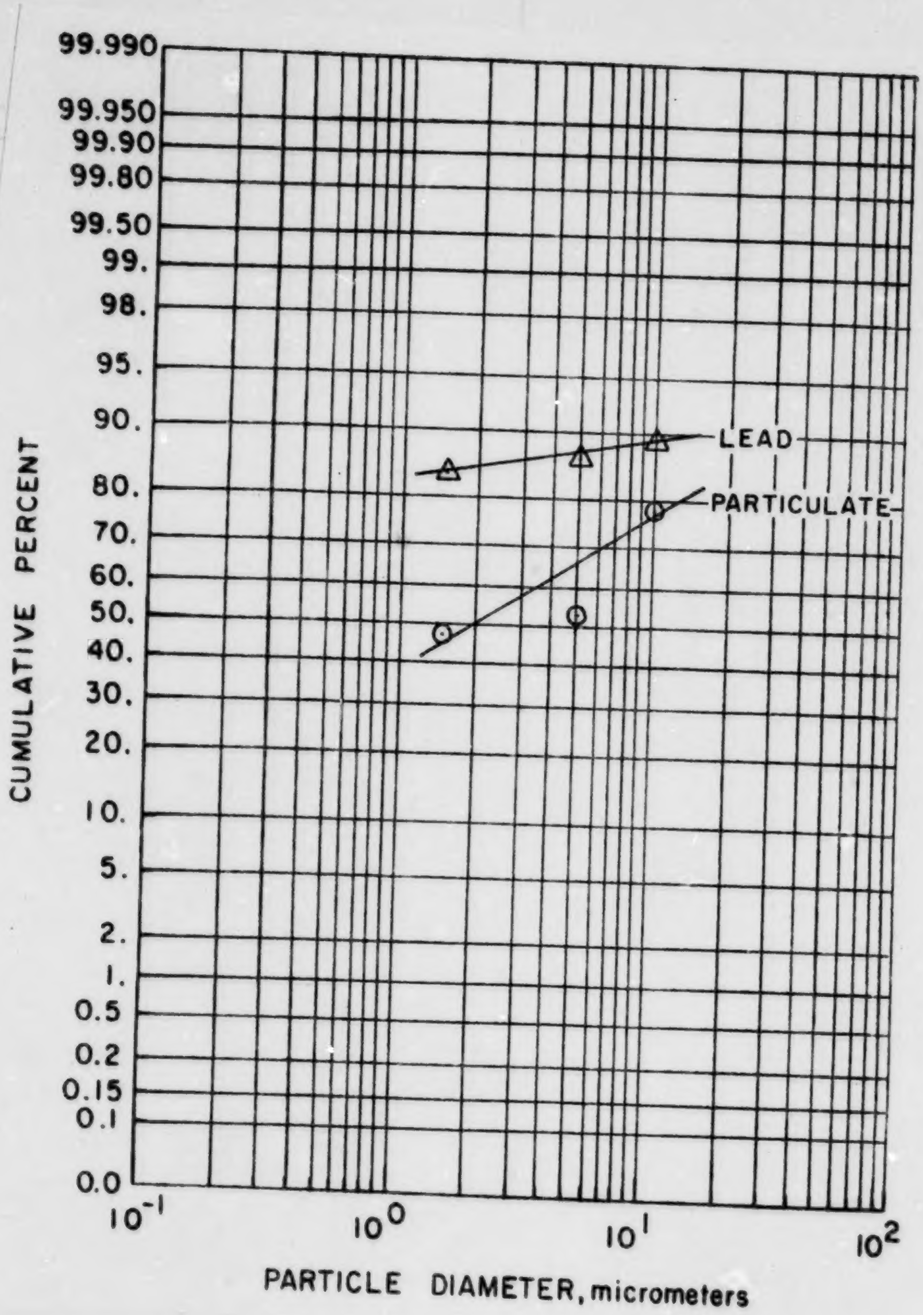


Figure 1. Particle size distribution Site A.

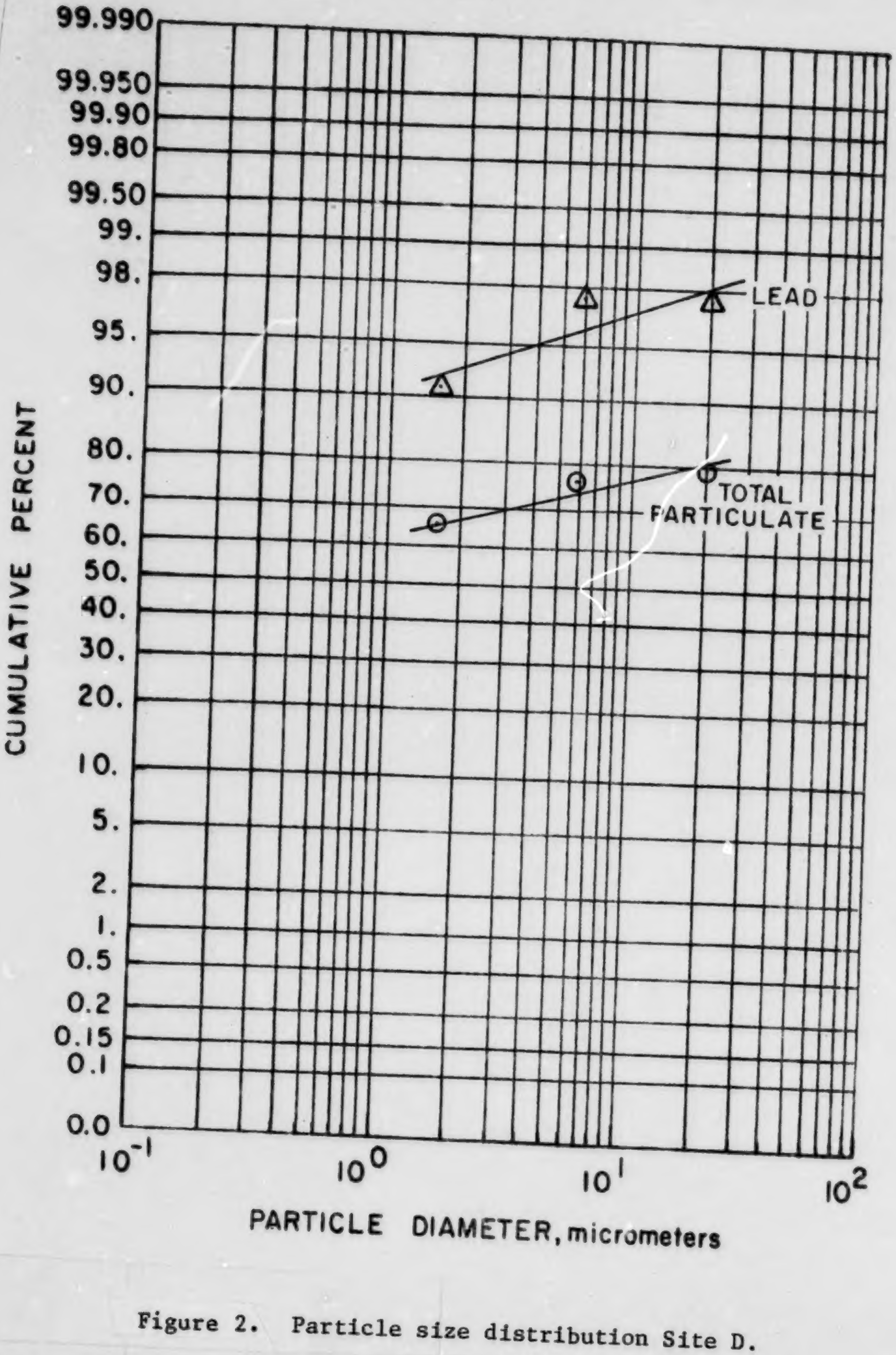
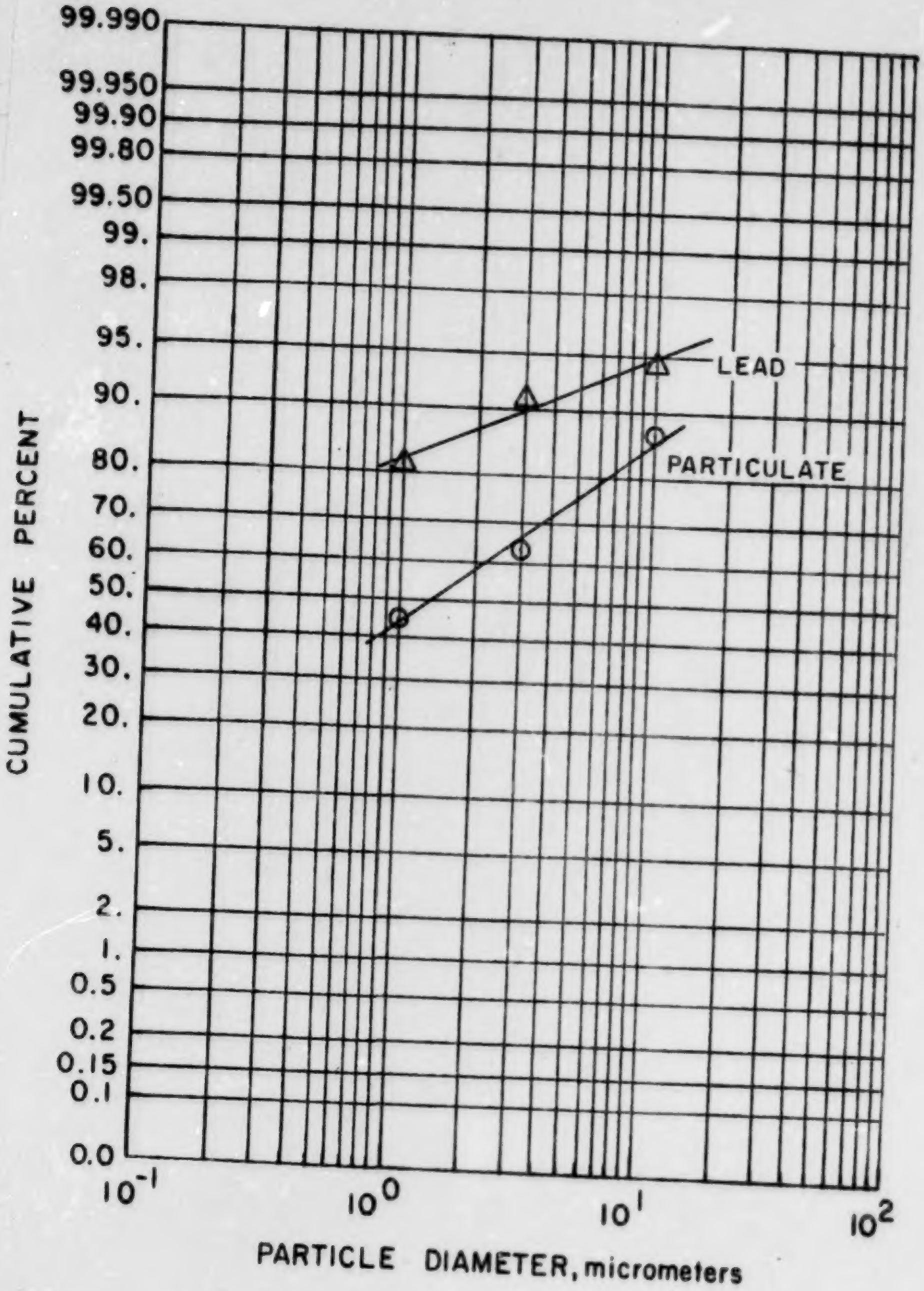


Figure 2. Particle size distribution Site D.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE

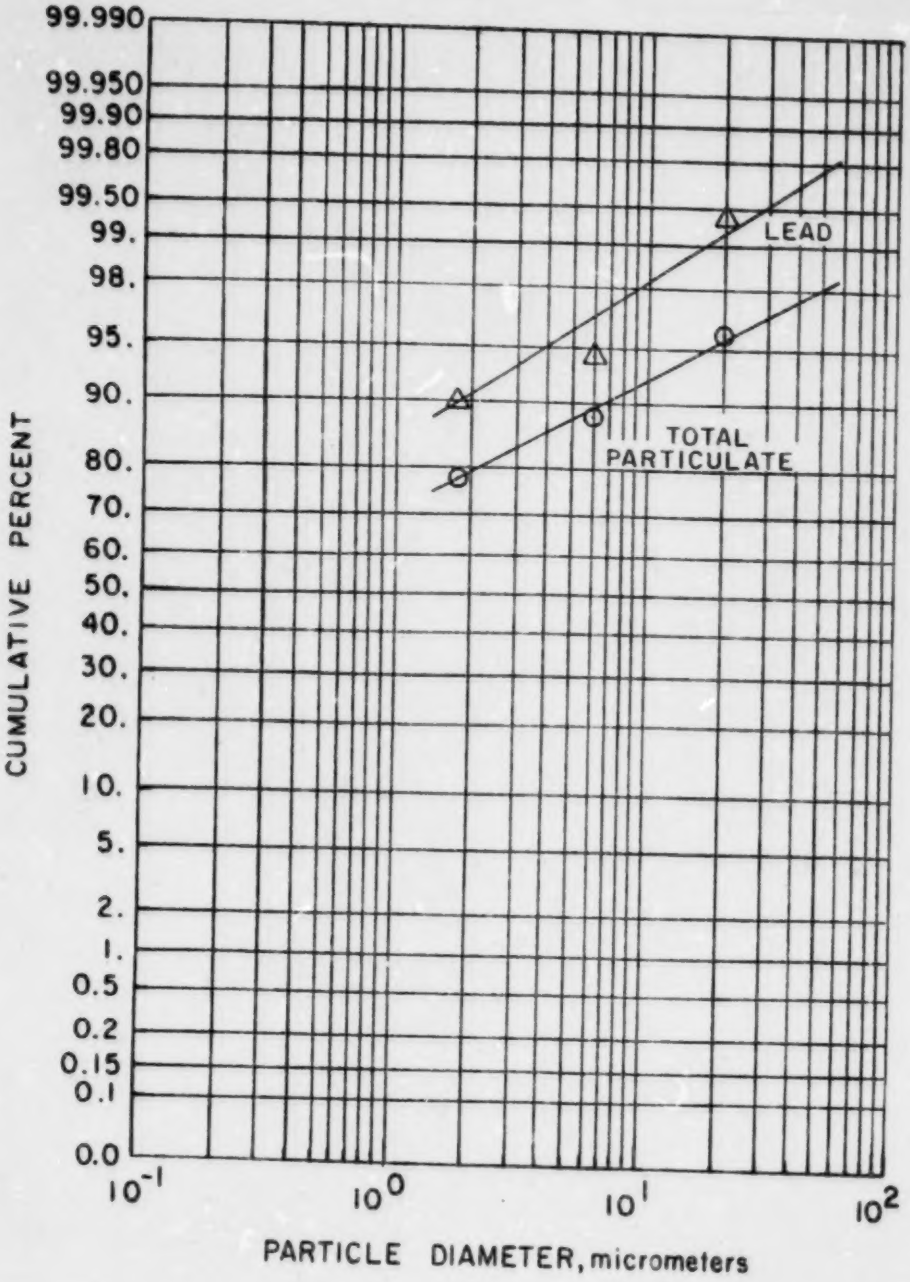


BEGIN LAST LINE OF TEXT

Figure 3. Particle size distribution Site E.

EPA-287 (Cin.)
(4-76)
PAGE NUMBER

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE



BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT

Figure 4. Particle size distribution Site G.

PAGE NUMBER
EPA-287 (Cin)
(4-75)

The results of the analysis of firetube ash samples collected from the boiler at Site D are presented in Table 4. Gravimetric determinations conducted on the collected fly ash indicated that 3.9 kg of ash was deposited in the tubes during the 5.3 hours of operation. Typically, boilers of this size firing waste fuels are cleaned on a weekly or biweekly basis. The lead and chloride values provide for material balance closures of 70 and 64 percent respectively for the fuel feed, fly ash, and flue gas streams at this site. In order to judge the extent to which the lead might leach from this fly ash. These samples were subjected to EP toxicity procedures. The results exceeded the allowable concentrations for two of the compounds, lead and cadmium and indicate that the fly ash from these combustion processes have the potential for being classified a hazard hazardous waste.

## ORGANIC COMPONENTS

### Volatile Organics

Destruction and removal efficiency (DRE) measurements were conducted for the following volatile organic compounds: chloroform, trichloroethane, trichloroethylene and perchloroethylene. The range of DRE's for these compounds for any individual test was 99.4 to 99.96 percent. The average DRE per test site ranged from 99.65 to 99.93 percent. Table 5 presents the average DRE values on a site by site basis. As indicated, similar degrees of destruction have been achieved for each of the compounds. This might have been anticipated from their close rankings on EPA hierarchy list of predicted incineration potential.[2]

There does not appear to be a clear relationship between the sizes of the boilers sampled, and the calculated destruction and removal efficiencies. The fact that similiar DRE's were calculated for sites D, E, F and G may, in part be due to the fact that the calculated heat inputs, based on the measured fuel feed for these sites (rated capacities 2.4 to 12 x $10^6$ Btu/hr) were very similar and ranged from 2.0 to 3.1 x $10^6$ Btu/hr.

Generally, the lowest DRE's were experienced at Site A, the only boiler rated at less than 1 x $10^6$ Btu/hr. The unit normally fires No. 2 fuel and proved not to be adaptable for waste fuels. Initial tests firing the spiked waste oil resulted in volatile organic concentrations of 1.2 percent in the flue gas with associated combustion efficiencies of 93 percent. Serious operational problems where experienced during these tests. It proved to be impossible to obtain the proper pressure to atomize waste fuel without flooding the relatively small combustion chamber of the 0.5 x $10^6$ Btu/hr boiler. Heat tracing of the fuel feed system improved the combustion efficiency to acceptable levels but extensive maintenance was required throughout each test due to clogging of the burner nozzle. Dilution of the waste fuel 50:50 with No. 2 fuel was required for acceptable operation. For these reasons, it would seem that the use of undiluted or poorly characterized waste oils in boilers of this size would not be practical, and would not be recommended under most circumstances.

TABLE 4a. INORGANIC ANALYSIS OF FIRETUBE FLYASH SAMPLES - SITE D

| | Concentration (μg/g) |
|---|---|
| Arsenic | 120 |
| Cadmium | 35 |
| Chromium | 110 |
| Lead | 24,200 |
| Zinc | 9,900 |
| Chloride | 12,100 |

TABLE 4b. EP TOXICITY TESTS ON FIRETUBE FLYASH SAMPLES

| | Leachate concentration (mg/l) | EP Toxicity Allowable (mg/l) |
|---|---|---|
| Arsenic | 1.2 | 5.0 |
| Cadmium | 1.6 | 1.0 |
| Chromium | 3.8 | 5.0 |
| Lead | 6.0 | 5.0 |

TABLE 5. DESTRUCTION AND REMOVAL EFFICIENCIES (PERCENT)

| Boiler Size ($10^6$ Btu/hr) | Boiler Sites A<br>0.5 | C<br>2.4 | D<br>2.7 | E<br>3.4 | F<br>4.2 | G<br>12.5 | Average by compound |
|---|---|---|---|---|---|---|---|
| Chloroform | 99.65 | 99.91 | 99.96 | 99.90 | 99.94 | 99.95 | 99.88 |
| Trichloroethane | 99.78 | 99.95 | 99.97 | 99.37 | 99.80 | 99.93 | 99.80 |
| Trichloroethylene | 99.45 | 99.92 | 99.89 | 99.85 | 99.92 | 99.87 | 99.82 |
| Perchloroethylene | 99.74 | 99.91 | 99.86 | 99.73 | 99.85 | 99.96 | 99.84 |
| Average by Site | 99.65 | 99.92 | 99.92 | 99.71 | 99.88 | 99.93 | 99.83 |

Note: Destruction and removal efficiencies are determined as follows:

$$\left[\frac{\text{(Feed Rate)} - \text{(Emissions Rate)}}{\text{(Feed Rate)}}\right] \times 100$$

There appears to be a general relationship between the DRE values and the associated combustion efficiencies presented earlier in Table 2, the lowest average combustion efficiency determined in the program, 99.03 percent, corresponds to an average DRE value of 99.73 and the three boilers operating with combustion efficiencies greater than 99.9 percent have associated DRE values that average 99.91 percent. An exception appears in the case of Site D, however, where a combustion efficiency of 99.36 percent corresponds to one of the higher DRE's measured (99.92 percent).

Feed rates to the boilers ranged from $6.7 \times 10^6$ to $5.6 \times 10^6$ g/hr, due primarily to the variations to the spike concentrations as presented in Appendix A. The atmospheric emission rates for these compounds, as summarized in Table 1, ranged from $1.1 \times 10^4$ to $1.7 \times 10^6$ g/hr. A "typical" site provided for approximate POHC feed rates and emission rates of $1.5 \times 10^8$ and $1.5 \times 10^5$ g/hr, respectively.

The principal terms in the DRE calculations are the concentrations of the compounds of interest in the waste feed and flue gas streams. The potential sampling and analytical error for these samples was determined, through the use of alternative analytical techniques and duplicate samples, to be 10 and 20 percent, respectively. The error of the GC/ECD analysis for these components in a gas matrix was determined to be less than $\pm 20$ percent using NBS traceable gas mixtures. The maximum effect of these factors on a DRE value of 99.90 percent was determined to be $\pm 0.04$ percent. Table 6 shows the concentration ranges in the stack gases for the compounds tracked throughout the program.

The Tenax samples collected with the VOST* were screened by GC/MS for additional volatile organic compounds considered to be potential products of incomplete combustion. The results of these analyses are presented in Appendix A. With the exception of benzene and toluene, which are known degradation products of Tenax resin, none of the detected combustion by-products are found in the Appendix VIII list of hazardous constituents and only two of the compounds, trichlorofluoro-methane and trichloropropanic acid, are chlorinated, indicating that chlorinated combustion by-products are not formed or, if formed, decompose very quickly.

---

*The VOST samples were collected in accordance with the procedures authored in the "Protocol for Collection and Analyses of Volatile POHCs using a Volatile Organic Sampling Train (VOST)," Envirodyne Engineers, April 1983. It should be noted that the monitoring of sample and resin temperatures are not required by this protocol. It is therefore not possible to accurately assess the collection efficiency of the resin.

TABLE 6. AVERAGE FLUE GAS CONCENTRATIONS OF THE VOLATILE AND SEMI-VOLATILE SPIKE COMPONENTS

| | ($\mu g/m^3$) | | | | | |
|---|---|---|---|---|---|---|
| | A | C | D | E | F | G |
| Volatile Components: | | | | | | |
| Chloroform | 110 | 120 | 44 | 53 | 88 | 153 |
| Trichloroethane | 90 | 88 | 22 | 580 | 400 | 140 |
| Trichloroethylene | 160 | 94 | 66 | 62 | 70 | 200 |
| Tetrachloroethylene | 160 | 200 | 180 | 220 | 170 | 100 |
| Semi-Volatile Components: | | | | | | |
| Trichlorobenzene | 48 | 20 | 75 | 51 | 48 | 89 |
| 1-chloronaphthalene | 16 | 12 | 22 | 23 | 36 | 89 |
| Trichlorophenol | 10 | 9 | -- | 16 | 6 | -- |

*Fuel feed ranges during the course of the program ranged generally from 3 to 30 gal/hr, depending on the size of the facility.

## Semivolatile Organics

The calculated destruction and removal efficiencies for the spiked semivolatile compounds for individual tests ranged from 99.84 to greater than 99.99 percent. The average DRE values from each site are presented in Table 7. These values generally correspond to flue gas concentrations of less than 100 μg/m$^3$. The ND (not detected) values obtained for trichlorophenol for many of the tests are due to the low concentrations of this component in the waste feed. The trichlorophenol used for spiking was solid in nature and could have been removed from the fuel stream by basket filters placed in the feed system. DRE values have not been presented for chlorotoluene as a result of analytical difficulties in obtaining acceptable waste feed results for this compound. At the midpoint of the program, chlorotoluene had been substituted for chlorophenol. The concentrations detected in the flue gas samples are consistent with those of the other semivolatile components and would indicate similar levels of removal.

The fact that the DRE values are generally higher for the semivolatile components than for the volatiles is consistent with their relative rankings on the "incineration" hierarchy list. The flue gas samples were screened for additional semivolatile compounds, considered to be products of incomplete combustion (PICs). A complete list of detected compounds are presented in Appendix A as Table 3 with each of the site data summaries. The majority of the compounds detected are known contaminants of XAD-2 resin and/or may be formed during the exposure of resin to combustion source flue gases. In general, the compounds detected in these analyses are polynuclear aromatics that are also found in traditional combustion sources.[13]

In several instances, however, phenol, chlorinated benzene and toluene species were detected at levels up to 730 μg/m$^3$. Dibenzofuran, a documented PIC in traditional combustion sources, was detected in the flue gas at each of the sites. The highest concentration, 200 μg/m$^3$, was detected at Site A, the smallest of the boilers tested. This value coincided with the lowest combustion efficiency, 98.3 percent, determined in the program. The remaining dibenzofuran levels ranged from less than 0.05 μg/m$^3$ to 70 μg/m$^3$. The average dibenzofuran values for each of the sites is presented in Table 8. The dibenzofuran concentrations are significant in that they demonstrate a potential to form the more highly toxic polychlorinated dibenzofuran (PCDF) and polychlorinated dioxins (PCDD). Detectable levels of these compounds were found in flue gas samples from 15 of the 25 samples analyzed. The concentration and speciation of these compounds are also presented in Table 8.

For chlorinated dioxin compounds, the concentration range encountered in approximately 0.2 to 17 μg/m$^3$. On a volume/volume basis, this corresponds to a range of 20 to 470 parts per trillion (PPT). These are very low concentration levels and not unexpected in view of the high chlorine content of the waste fuel.

### TABLE 7. DESTRUCTION AND REMOVAL EFFICIENCIES FOR THE SEMIVOLATILES SPIKE COMPOUNDS (PERCENT)

| Boiler Size ($10^6$ Btu/hr) | A | C | D | E | F | G | Average by Compound |
|---|---|---|---|---|---|---|---|
| | 0.5 | 2.4 | 2.7 | 3.4 | 4.2 | 12.5 | |
| Trichlorobenzene | 99.84 | 99.98 | 99.96 | 99.90 | ≥99.96 | 99.89 | ≥99.92 |
| 1-chloronaphthalene | 99.95 | 99.99 | 99.95 | ≥99.94 | ≥99.98 | 99.92 | ≥99.95 |
| Trichlorophenol | ≥99.97 | ≥99.99 | - | ≥99.92 | ≥99.98 | - | ≥99.97 |
| Average by Site | ≥99.92 | ≥99.99 | 99.96 | ≥99.92 | ≥99.97 | 99.91 | |

TABLE 8. AVERAGE CONCENTRATIONS IN STACK GAS OF DIBENZOFURAN AND DIOXIN SPECIES FROM TESTS EXHIBITING DETECTABLE LEVELS ($\mu g/m^3$)

| | A$^a$ | C$^c$ | D$^a$ | E$^a$ | F$^a$ | G$^b$ |
|---|---|---|---|---|---|---|
| Dibenzofuran | 62(5) | 5.4(2) | 3.4(5) | 8.0(5) | 16(3) | 2.7(3) |
| Chlorodibenzofuran | 0.8(3) | 0.52(1)$^d$ | 0.7(3) | 0.4(2) | 2.1(1)$^d$ | |
| Dichlorodibenzofuran | 1.9(2) | 0.07(1) | | 0.24(1) | | |
| Trichlorodibenzofuran | | 0.43(2) | | | | |
| Tetrachlorodibenzofuran | | | | 0.17(1) | | |
| Dibenzodioxin | 1.3(3) | | | 0.73(1) | | |
| Chlorodibenzodioxin | | 0.27(1) | | | | |
| Dichlorodibenzodioxin | | 0.18(1) | | 1.6(1) | 2.4(1) | |
| Tetrachlorodibenzodioxin | | | | | | 1.4(1) |
| Octachlorodibenzodioxin | | 4.5(1)$^d$ | | | 17(1)$^d$ | |

[a] Samples from 5 tests analyzed.

[b] Samples from 3 tests analyzed.

[c] Samples from 2 tests analyzed.

[d] Quality assurance samples indicate potential loss, see Section 6.

( ) number of tests in which component was detected.

Tests were specifically conducted for tetrachlorodibenzodioxin (TCDD), which is generally acknowledged to be the most toxic of the chlorinated dioxin isomers. As shown in Table 9, trace levels (1.4 $\mu g/m^3$ - equivalent to 100 ppt) appeared in only one test run; this occurred at Site G. The complete results of the dibenzofuran/dioxin analysis are presented in Appendix A as Table 4 with each of the Site Data Summaries.

At one of the sites (Site D), ash trapped in the firetubes of the boiler was removed and analyzed for chlorinated dibenzodioxin compounds. Parts per billion by weight (ppb) levels of TCDF's and TCDD's were detected in the firetube ash sample collected at site D. The results of these analyses are presented in Table 10.

Tests were conducted on the basestock waste oil with and without the "spiked" contaminants to determine if trace levels of chlorinated dioxins or chlorinated dibenzofurans in the waste oil or the chemicals spiked into the waste oil were responsible for the chloro-dioxins and chloro-dibenzofurans which appeared in the stack gas. Chlorinated dibenzo-dioxins and chlorinated dibenzofurans were not detected in either the basestock or the spiked oil; the detection limits for the various isomers are shown in Table 11.

No tetrachlorodibenzodioxin (TCDD) compounds were detected. Chlorinated dibenzofuran compounds were more prevalent than chlorinated dibenzodioxins. Several isomers were present at concentrations of several hundred parts per billion (ppb - by weight).

## CONCLUSIONS

Although a sample population of six boilers is somewhat limited to provide definitive results applicable to all commercial boilers, it is possible to state several general conclusions regarding the combustion of waste automotive fuels.

1. It is possible to achieve combustion efficiencies greater than 99.9 percent for commercial boilers firing waste oils. It may not be practical, however, to burn undiluted or poorly characterized waste fuels in smaller boilers due to the excessive maintenance required.
2. Destruction and removal efficiencies of greater than 99.9 percent can be obtained for several chlorinated organic contaminants typically present in waste oils. For the volatile compounds studied, chloroform, trichloroethylene, trichloroethane, and perchloroethylene, destruction efficiencies were on the order of 99.9 percent. For the semivolatile compounds, trichlorobenzene, 1-chloronaphthalene, trichlorophenol, destruction efficiencies were on the order of 99.95 percent.
3. For boilers above 1 x $10^6$ Btu/hr input, there were no apparent correlations between boiler size and firing method and destruction efficiency.

TABLE 9. SEMIVOLATILE ANALYSIS OF FIRETUBE ASH, SITE D (μg/kg)

| | First pass sample | Second pass sample | Third pass sample | Cleaning trap sample |
|---|---|---|---|---|
| Trichlorobenzene | 820 | 340 | 340 | 250 |
| 1-chloronaphthalene | 330 | 29 | ND | ND |
| Chlorotoluene | ND | ND | ND | ND |
| Naphthalene | 1300 | 1100 | 1700 | 740 |
| Anthracene/Phenanthrene | 1100 | 2000 | 1100 | 2100 |
| Chrysene/Benz(a)anthracene | 140 | 1400 | 150 | - |
| Benzo(b)fluoranthene/benzo(k)fluoranthene | - | 57 | 16 | - |
| Fluorene | 230 | - | 180 | - |
| Pyrene | 86 | 300 | 39 | - |
| Naphthalene, methyl isomers | 2000 | 1500 | 1200 | 1100 |
| Naphthalene alkyl $C_{12}H_{12}$ isomers | 2600 | 1100 | 610 | 880 |
| Naphthalene alkyl $C_{12}H_{14}$ isomers | 5900 | 2500 | - | 2800 |
| Benzocinnaline | - | 2500 | - | 1300 |
| Naphthopyrandione isomers | - | 3700 | 2400 | 3300 |
| Phenanthrene-methyl isomers | - | 4900 | - | 4200 |
| 7(H)-Benz(d)anthracene-7-one | - | - | - | 840 |
| 4H-1-Benzopyran-4-one | 780 | 420 | - | 240 |
| Benzofuran | - | 550 | - | - |
| 9(10H)anthracenone | 240 | 590 | - | 450 |
| 910 anthracenedione | - | - | - | 1300 |
| Biphenyl | 190 | 70 | 120 | - |
| Dibenzethraphene | 360 | 460 | 290 | 440 |
| Dibenzothraphene, methyl isomers | - | - | - | 390 |
| 1,3-Isobenzofurandione | 230 | 450 | 410 | 400 |
| 2-Propanol, 2-(2-methoxy-1-methyl ethoxy) | - | - | - | 82 |
| 9-H-Fluorene-9-one | - | - | - | 1500 |
| Phenol,2,6-bis(1,1-dimethyl ethyl)-4 ethyl | - | - | - | 80 |

TABLE 10. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS, SITE D - FLY ASH (μg/kg)

| Component | First pass sample | Second pass sample | Third pass sample | Cleaning trap sample | Det. limit (NDI) |
|---|---|---|---|---|---|
| Dibenzofuran | 250 | 170 | 24 | 230 | 0.5 |
| Chlorodibenzofuran | ND | 24 | ND | ND | 0.5 |
| Dichlorodibenzofurans | ND | ND | ND | ND | 0.5 |
| Trichlorodibenzofurans | ND | ND | ND | ND | 0.5 |
| Tetrachlorodibenzofurans | 350 | 170 | 11 | 160 | 0.5 |
| Pentachlorodibenzofurans | 1000 | 660 | 60 | 35 | 2 |
| Hexachlorodibenzofurans | 230 | 310 | ND | 250 | 2 |
| Heptachlorodibenzofurans | 580 | 340 | ND | 160 | 5 |
| Octachlorodibenzofurans | 40 | 26 | ND | ND | 10 |
| Dibenzodioxin | ND | ND | ND | ND | 0.5 |
| Chlorodibenzodioxins | ND | ND | ND | ND | 0.5 |
| Dichlorodibenzodioxins | ND | ND | ND | ND | 0.5 |
| Trichlorodibenzodioxins | ND | ND | ND | ND | 0.5 |
| Tetrachlorodibenzodioxins | ND | ND | ND | ND | 0.5 |
| Pentachlorodibenzodioxins | 120 | 58 | ND | ND | 2 |
| Hexachlorodibenzodioxins | 200 | 90 | ND | ND | 2 |
| Heptachlorodibenzodioxins | 230 | 130 | ND | ND | 5 |
| Octachlorodibenzodioxins | 33 | 150 | ND | 70 | 10 |

TABLE 11. DIOXIN AND DIBENZOFURAN CONTENT OF WASTE OIL BASESTOCK AND "SPIKED" WASTE OIL

| Component | Sample ID | Oil*<br>22033<br>W-BSB-1 | Waste Oil Basestock<br>22034<br>W-BS-1 | Typical "Spiked" Waste Oil<br>290507-1<br>WO-C-3-WFC | Detection Limit (mg/kg) (ND = < ) |
|---|---|---|---|---|---|
| dibenzofuran | ND | ND | ND | ND | 0.04 |
| chlorodibenzofurans | ND | ND | ND | ND | 0.08 |
| dichlorodibenzofurans | ND | ND | ND | ND | 0.10 |
| trichlorodibenzofurans | ND | ND | ND | ND | 0.20 |
| tetrachlorodibenzofurans | ND | ND | ND | ND | 0.20 |
| pentachlorodibenzofurans | ND | ND | ND | ND | 0.40 |
| hexachlorodibenzofurans | ND | ND | ND | ND | 0.40 |
| heptachlorodibenzofurans | ND | ND | ND | ND | 0.80 |
| octachlorodibenzofurans | ND | ND | ND | ND | 2.0 |
| dibenzodioxin | ND | ND | ND | ND | 0.04 |
| chlorodibenzodioxins | ND | ND | ND | ND | 0.08 |
| dichlorodibenzodioxins | ND | ND | ND | ND | 0.10 |
| trichlorodibenzodioxins | ND | ND | ND | ND | 0.20 |
| tetrachlorodibenzodioxins | ND | ND | ND | ND | 0.20 |
| pentachlorodibenzodioxins | ND | ND | ND | ND | 0.40 |
| hexachlorodibenzodioxins | ND | ND | ND | ND | 0.40 |
| heptachlorodibenzodioxins | ND | ND | ND | ND | 0.80 |
| octachlorodibenzodioxins | ND | ND | ND | ND | 2.0 |

No. 4 Oil A

*No. 4 oil provided for reference purposes.

4. Inorganic components, principally lead and hydrochloric acid, and particulate matter constitute the most significant atmospheric emissions resulting from the combustion of waste oils comprised primarily of automotive waste oils. The particulate lead emissions from a source may, during the peak heating season, affect the compliance with the primary ambient air standard.

5. The presence of measurable levels of dibenzofurans in the flue gases of the boilers indicates the potential for the emission of polychlorinated dibenzofuran and dioxin species at parts per billion levels. These types of compounds were not present in the waste feed; hence, the conclusion is that they most likely formed at trace levels during the combustion process.

6. The fly ash deposited in the firetubes of the boilers may contain percent levels of lead and parts per billion levels of dibenzofuran and dioxin species. The ash has the potential for being classified as hazardous on this basis, and may be subject to hazardous waste regulations for disposal.

# REFERENCES

1. Surprenant, N., et al. Emissions Assessment of Conventional Stationary Combustion Systems, Volume IV. EPA-600/7-79-0291.

2. Turner, D. B. Workload of Atmospheric Dispersion Estimates. U.S. Department of Health, Education and Welfare, Public Health Service. Cincinnati, OH. 1969.

3. Hansen, R. L., et al. Chemical Characterization of Polynuclear Aromatic Hydrocarbon Airborne Effluents from an Experimental Fluidized Combustion. Presented at the Fourth International Symposium on Polynuclear Aromatic Hydrocarbons. Battelle Columbus Laboratories. October 1979.

# SECTION 3

# SELECTION OF TEST BOILERS

## OIL-FIRED COMMERCIAL/INDUSTRIAL BOILER POPULATION

The boiler population under investigation in this study includes oil-fired boilers with heat input capacities below 20 x $10^6$ Btu/hr, with boilers smaller than 10 x $10^6$ Btu/hr being emphasized. The size range of 1.5 to 10 x $10^6$ Btu/hr represents 43 percent of the commercial boilers currently installed in the U.S. Table 12 presents a breakdown of the commercial boiler population classified according to size and heat transfer methods.[1]

Three heat transfer methods: firetube, water tube, and cast iron are used in boilers in this size range.

## MAJOR CLASSIFICATIONS OF BOILER DESIGN

An overview of all boilers smaller than 25 x $10^6$ Btu/hr shows that firetube units account for 52 percent of capacity, cast iron boilers account for 37 percent and water tube boilers account for 11 percent. Cast iron boilers dominate the small end of the size range while firetube boilers are most common in the other three size ranges. Residual oil represents about 60 percent of the fuel use (assuming that fuel use is proportional to capacity) and distillate oil represents the remaining 40 percent of oil consumption.

### Cast Iron Boilers

Cast iron boilers are used in domestic or small commercial operation to produce either low-pressure steam or hot water. Capacities range from 0.003 up to 14 x $10^6$ Btu/hr heat input. Commercial cast iron boilers are usually square or rectangular and consist of several vertical sections. Water enters each section at the bottom and the steam or hot water exits from the top. In each section the combustion gases pass through a maze of tubes. These tubes transfer heat from the gas to the water. The capacity of the commercial cast iron boiler is determined by the number of sections.

### Firetube Boilers

Scotch and firebox (short firebox and compact) are the most common types of firetube boilers, each representing about 40 percent of installed firetube capacity. Horizontal return tubular boilers used to be very popular but now account for only 10-15 percent of capacity.

## TABLE 12. OIL-FIRED COMMERCIAL/INDUSTRIAL BOILER CHARACTERISTICS[1]

| Parameter | Fuel capacity | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0.4 x $10^6$ Btu/hr | | | 0.4-1.5 x $10^6$ Btu/hr | | | 1.5-10 x $10^6$ Btu/hr | | | 10-25 x $10^6$ Btu/hr | | |
| | Cast iron | Fire tube | Water tube | C.I. | F.T. | W.T. | C.I. | F.T. | W.T. | C.I. | F.T. | W.T. |
| Number of distillate oil-fired boilers (1000) | 127.8 | - | - | 45.0 | 30.2 | 2.9 | 15.2 | 14.1 | 3.0 | - | 3.3 | 0.7 |
| Number of residual oil-fired boilers (1000) | 203.6 | - | - | 71.6 | 46.3 | 1.1 | 24.3 | 21.5 | 3.2 | - | 5.1 | 2.7 |
| Capacity of distillate oil-fired boilers (1000 MW) | 9.4 | - | - | 10.1 | 8.9 | 1.0 | 14.2 | 22.7 | 3.5 | - | 17.1 | 3.0 |
| Capacity of residual oil-fired boilers (1000 MW) | 15.0 | - | - | 16.1 | 13.6 | 0.4 | 22.7 | 34.6 | 4.8 | - | 26.1 | 13.0 |
| Fraction of total commercial oil capacity (%) | 3.98[a]<br>6.35[b] | -<br>- | -<br>- | 4.28<br>6.82 | 3.77<br>5.76 | 0.42<br>0.16 | 6.01<br>9.61 | 9.61<br>14.65 | 1.48<br>2.03 | -<br>- | 7.24<br>11.0 | 1.27<br>5.50 |

[a] Distillate oil

[b] Residual oil

The burner flame in a Scotch boiler is contained in an elongated, water cooled combustion chamber which also acts as the first pass for heat transfer.[2] This characteristic is unique to this type of boiler.[2] Two-, three-, or four-pass units are available as indicated in Figure 5.[3] The rear wall of the furnace is either refractory-lined ("dry-back") or water-cooled ("wet-back") in the later versions. Due to the relatively small diameter firetubes and concomitant large pressure drop, they require provision for mechanical draft.[2]

Most Scotch boilers are designed with a minimum amount of heating surface. Improved heat transfer is obtained by the following design features:[2]

- High flue gas velocities throughout the boiler due to the use of a steadily diminishing number of constant-diameter firetubes in each subsequent pass
- Turbulators in the firetubes
- Improved water-side circulation by internal baffling and other means

Seven boilers were designated for testing in the program. The units were selected so as to provide a representative cross section of the commercial boiler population. A listing of the boilers by rated capacity is presented in Table 13.

## BOILER OPERATING CONDITIONS

### Load Variability

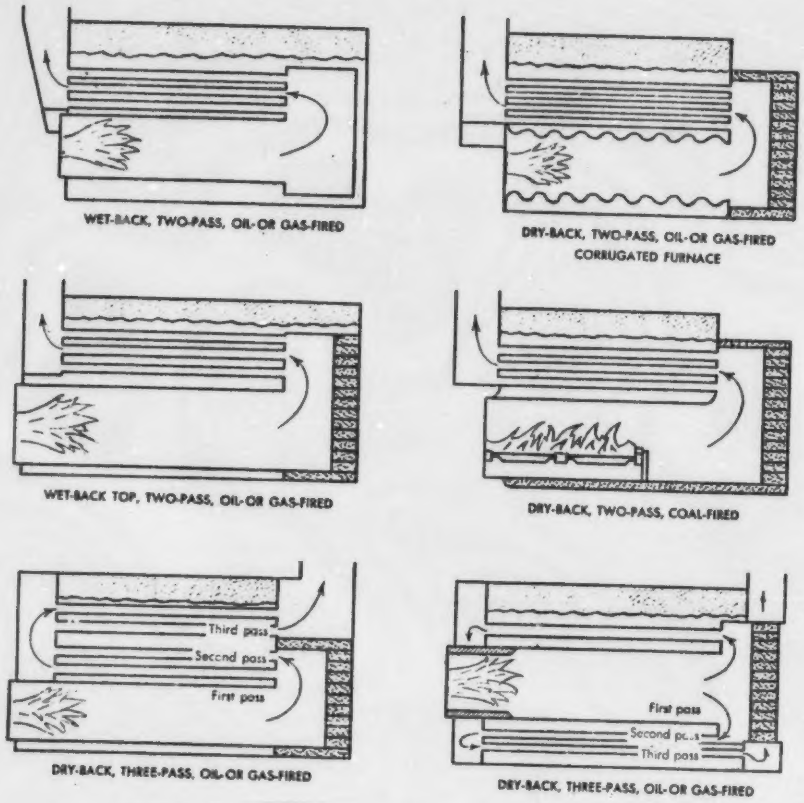
Boilers in the size range under investigation in this study are typically operated in the on-off mode and at variable loads. Load variability is achieved through modulation of fuel flow rate. Investigation of residential systems operating in on-off mode has shown high hydrocarbon emission rates at the beginning and end of the cycle (see Figure 6).[2] The peak emission rates noted in Figure 7 may be responsible for most of the total emissions. For this reason, the sampling periods at each site were arranged to cover startup and shutdown cycles.

Newer and larger boilers tend to operate at variable loads rather than in the on-off mode. Data on typical operating modes and the prevalance of load modulation are not available. During the winter some facilities will operate with one boiler at full load and a second in the on-off mode. The most modern and efficient units will operate at variable loads.

### Fuel Atomization

Four oil atomization methods--air, steam, mechanical or pressure, and rotary--can be used in the boiler size range under investigation. Air, rotary, and mechanical atomization were found to be common for firing waste oil in the boiler size ranges under investigation.

Reproduced from best available copy.



WET-BACK, TWO-PASS, OIL-OR GAS-FIRED

DRY-BACK, TWO-PASS, OIL-OR GAS-FIRED CORRUGATED FURNACE

WET-BACK TOP, TWO-PASS, OIL-OR GAS-FIRED

DRY-BACK, TWO-PASS, COAL-FIRED

DRY-BACK, THREE-PASS, OIL-OR GAS-FIRED

DRY-BACK, THREE-PASS, OIL-OR GAS-FIRED

Third pass
Second pass
First pass
First pass
Second pass
Third pass

Figure 5. Gas flow in Scotch boiler types.

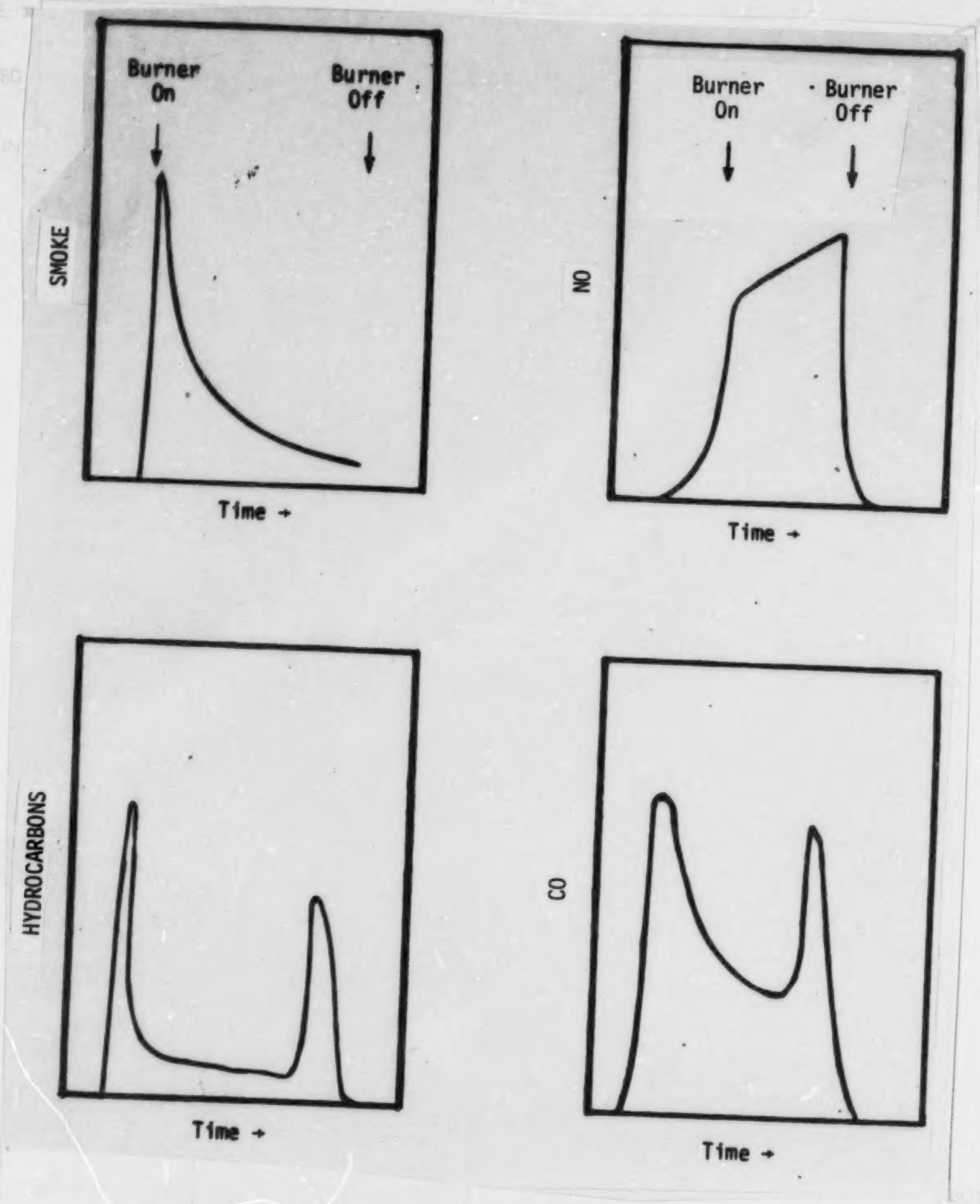
3-1

TABLE 13. BOILER DESCRIPTIONS

| Site description | Boiler rated capacity $10^6$ BTU/hr | Boiler type | Method of atomization | Site description |
|---|---|---|---|---|
| A | 0.5 | cast iron | mechanical | office building |
| B[a] | 1.0 | scotch fire-tube 2 pass | rotary cup | dairy complex |
| C | 2.4 | horizontal return tube | rotary cup | greenhouse |
| D | 2.7 | scotch fire-tube 3 pass | air | office building |
| E | 3.4 | scotch fire-tube 4 pass | rotary cup | greenhouse |
| F | 4.2 | scotch fire-tube 3 pass | air | greenhouse |
| G | 12.5 | scotch fire-tube 4 pass | air | greenhouse |

[a] Boiler not available for testing in the program due to problems with the burner assembly and fuel feed system.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
TOP OF IMAGE AREA
DROPPED HEAD BEGIN SECTION HERE



BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSIONS FOR TABLES AND ILLUSTRATIONS

Figure 6. Characteristic emissions of residential oil burners during one complete cycle.

PAGE NUMBER

Rotary cup burners utilize a rotating cup to atomize the fuel. The oil is introduced into the cup where the centrifugal force causes the oil to form a thin film and move to the lip of the cup at which point it is distributed in the combustion zone as small droplets. While rotary burners are being phased out for traditional combustion applications, their use is common for the combustion of waste oils.

Steam and air atomization are very similar. Most air atomizers in the commercial sector are high pressure units. Oil flows through a central tube in the nozzle while the air (or steam) flows through an annular passageway around the oil passageway as shown in Figure 7.[6] Violent mixing, either inside or outside the nozzle, atomizes the oil into fine droplets. Steam-atomized burners are identical to air-atomized burners. When high pressure steam is readily available, it can be used to eliminate the need for an air compressor.

High pressure mechanical atomization accounts for the majority of domestic units and a large percentage of the small commercial units. Oil is supplied at about 150 psig to one or more orifices in the nozzle. The design of the orifice influences the spray pattern and, to some degree, the droplet size. The flow channel to the orifice is routed in such a way as to impart a high degree of swirl to the exiting oil. Combustion air, which flows in an annular region around the gun, is also given swirl before it mixes with the fuel spray outside the nozzle.

In general, any oil up to and including No. 6 can be atomized by the above methods as long as preheat is applied to bring the viscosity into the correct range. The usual ranges for firing viscosity are presented in Table 14.

TABLE 14. REQUIRED FUEL VISCOSITY FOR VARIOUS ATOMIZATION METHODS

| | Usual range of firing viscosity | |
|---|---|---|
| Atomization method | Saybolt Seconds Universal | Equivalent kinematic viscosity, centistokes |
| Pressure | 35-150 SSU | 4-32 cs |
| Steam or air | 35-250 SSU | 4-55 cs |
| Rotary | 150-300 SSU | 32-60 cs |

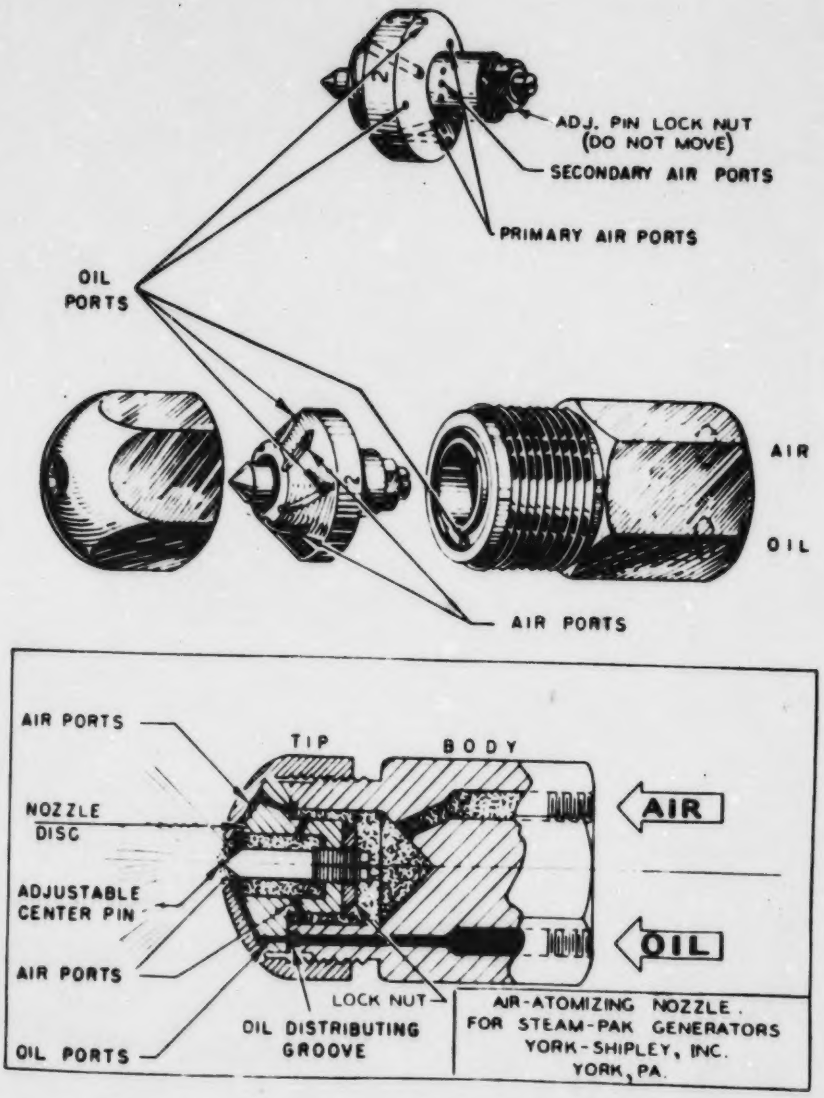

ADJ. PIN LOCK NUT
(DO NOT MOVE)
SECONDARY AIR PORTS
PRIMARY AIR PORTS
OIL PORTS
AIR
OIL
AIR PORTS
AIR PORTS
TIP
BODY
NOZZLE DISC
AIR
ADJUSTABLE CENTER PIN
OIL
AIR PORTS
LOCK NUT
OIL DISTRIBUTING GROOVE
OIL PORTS
AIR-ATOMIZING NOZZLE.
FOR STEAM-PAK GENERATORS
YORK-SHIPLEY, INC.
YORK, PA.

Figure 7. Air atomization nozzle.

# REFERENCES

1. Devitt, T., P. Spaite, L. Gibbs. Population and Characteristics/ Industrial/Commercial Boilers in the U.S. Prepared by PEDCo Environmental Inc. for the U.S. Environmental Protection Agency. Report No. EPA-600/7-79-178a, August 1979.

2. Offen, G. R., et al. Control of Particulate Matter from Oil Burners and Boilers. Prepared by Acurex Corporation for the U.S. Environmental Protection Agency. Report No. EPA-450/3-76-005, 1976.

3. Shields, C. D. Boilers: Types, Characteristics and Functions. McGraw-Hill Book Company, New York, NY, 1961.

4. Hall, R. E., J. H. Wasser, E. E. Berkay. A Study of Air Pollutant Emissions from Residential Heating Systems. U.S. Environmental Protection Agency, Report No. RPA-650/2-74-003, January 1974.

5. Guidelines for Burner Adjustments of Commercial Oil-Fired Boilers. Prepared by Battelle Columbus Laboratories for the U.S. Environmental Protection Agency, Report No. EPA-600/2-76-088, 1976.

6. Application, Installation, Starting, Operation and Maintenance of York Power Steam-Pak Steam Generators. York-Shipley Inc., York, Pennsylvania, 1959.

## SECTION 4

## FIELD ACTIVITIES

In order to maintain a consistent supply of waste fuel for the entire program, GCA purchased a 4000 gal lot of used automotive oil. A complete analysis of the oil for physical characteristics as well as principal chemical contaminants was conducted. The results of these analyses are presented in Table 15. Comparative values obtained from samples of No. 4 fuel oil and additional waste oil samples are also presented.

TABLE 15. CHARACTERIZATION OF THE BASESTOCK OIL

| Parameter | Waste oil basestock | Waste oil survey[a] | No. 4 fuel oil |
|---|---|---|---|
| Ash % | 0.67 | 0.13 - 1.3 | 0.03 |
| Sulfated ash % | 1.37 | 0.1 - 1.2 | 0.09 |
| Chlorine % | 0.20 | 0.05 - 2.7 | 0.01 |
| Sulfur % | 0.48 | 0.37 - 0.75 | 0.64 |
| Specific gravity (API) | 26.8 | 24.2 - 41.2 | 25.7 |
| Water % | 10.0 | 0.2 - 11.4 | -- |
| Viscosity SUS @ 100°F | 152.6 | 66 - 296 | 96.8 |
| Density lbs/gal | 7.443 | -- | 7.495 |
| Heating value BTU/gal | 122,670 | -- | 143,000 |
| Lead (ppm) | 1420 | 23 - 2000 | 0.8 |

[a] Values obtained from 24 samples of automotive waste oil.

The basestock oil was maintained under separate storage by the supplier at a licensed facility for the duration of the program. The appropriate volume of oil was delivered to each sampling site in 55 gallon containers.

Portions of the basestock oil were "spiked" with predetermined amounts of selected organic compounds which are typically found in a waste oil. The seven compounds selected are as follows:

- chloroform
- 1,1,1-trichloroethane
- trichlorobenzene
- 1-chloronaphthalene

- trichloroethylene
- tetrachloroethylene
- 2,4,5-trichlorophenol

Three of the four volatile compounds, trichloroethane, trichloroethylene, and tetrachloroethylene are widely used in industry in degreasing applications and routinely found in waste oils in the 1,000 ppm range.[1] The remaining volatile compound, chloroform, and the semivolatile trichlorobenzene, 1-chloronaphthalene and 2,4,5-trichlorophenol were selected as a result of their positions on the EPA list of hazardous constituents. About midway in the program, 2,4,5-trichlorophenol was replaced by chlorotoluene. The chlorophenol compound was a solid material and difficult to mix into the waste oil. Table 16 presents the heats of combustion of these compounds and provide their relative position in the EPA Hierarchy of Waste Incinerability with the lower ranking corresponding to the more difficult compound to destroy.

TABLE 16. EPA HIERACHY OF WASTE INCINERABILITY[2]

| Compound. | Heat combustion kcal/gm | Position ranking |
|---|---|---|
| Chloroform | 0.75 | 7 |
| Tetrachloroethylene | 1.19 | 11 |
| Trichloroethylene | 1.74 | 22 |
| Trichloroethane | 1.99 | 25 |
| 2,4,5 trichlorophenol | 2.88 | 50 |
| Trichlorobenzene | 3.40 | 64 |
| 1-chloronaphthalene | 7.37 | 206 |

The use of 2,4,5 trichlorophenol was also discontinued at Sites D and G due to its potential to form chlorinated dioxins and chlorinated dibenzofurans in combustion gas matrices. The compound was replaced with o-chlorotoluene (heat of combustion 6.92 kcal/gm, positive ranking 191), at these sites.

The "spike" components were introduced into the basestock fuel while on location at each of the sampling sites. In this manner the transportation of hazardous materials could be eliminated. The appropriate concentrations of "spike" and basestock materials was determined for each site using calculations involving the fuel feed rate, volumetric flow rate of the flue gas, the estimated destruction efficiency of the unit and the anticipated length of the sampling period.

The spike levels of the organic species of interest were varied at several of the sites to determine the effect of these various concentrations on the boilers combustion and destruction efficiencies. In summary, the testing was performed as follows:

| Site | Rated capacity $10^6$ Btu/hr input | Spike level of each component (ppm) | Total number of test runs |
|---|---|---|---|
| A | 0.5 | 1,500, 3,000 | 6 |
| C | 2.4 | 3,000 | 3 |
| D | 2.7 | 3,000, 10,000 | 6 |
| E | 3.4 | 3,000, 5,000 | 6 |
| F | 4.2 | 3,000, 5,000 | 6 |
| G | 12.5 | 3,000, 10,000 | 4 |

An additional "background" test was performed at Site D. This test was conducted firing No. 4 fuel oil and provides data to compare the combustion byproducts of waste oils to those of more traditional fuels. The results of this test are presented in Appendix D.

## OIL FEED SYSTEM

The waste fuel was maintained at the test site in 55 gallon drums. A portable drum stirrer was used initially to mix the spike components with the fuel. During the test runs, continued mixing was accomplished using the boilers recirculating pumps. A schematic of the basic fuel feed system used in the program is presented in Figure 8.

The fuel feed flow was monitored continuously throughout the test runs by an in-line flow meter and by physical measurements of the change in oil level in the mixing drum.

## OIL SAMPLING

Samples of the "as-fired" waste oil were obtained by means of a tap in the fuel feed line just prior to the burner. Samples were collected at 30-minute intervals during the sampling period. A 200-ml sample was collected and composited in a precleaned 1-gal amber glass container for subsequent organic and inorganic chemical analysis. In addition, samples were collected for volatile organic analysis in Volatile Organic Analysis (VOA) vials. Duplicate VOA samples were collected at 30-minute intervals during the sampling period.

### Fire Tube Fly Ash Sampling

Representative samples of fly ash deposited trapped in the firetubes were collected at Site D, a facility where it was possible to isolate the boiler so that only the spiked waste oil would be fired during the entire test period at the site, normally 3 days. Site D was the only facility where the overnight heat requirements permitted such isolation.

Prior to the initiation of testing at this site, the firetube sections of the boiler were cleaned of any residual fly ash. The boiler was cleaned again at the conclusion of the test program and the samples recovered to provide representative samples of the fly ash generated while firing waste oil. These samples were analyzed for metal content, total chloride, the chemical compounds spiked into the oil. They were also screened for products of incomplete combustion, including chlorinated dioxin and dibenzofuran compounds.

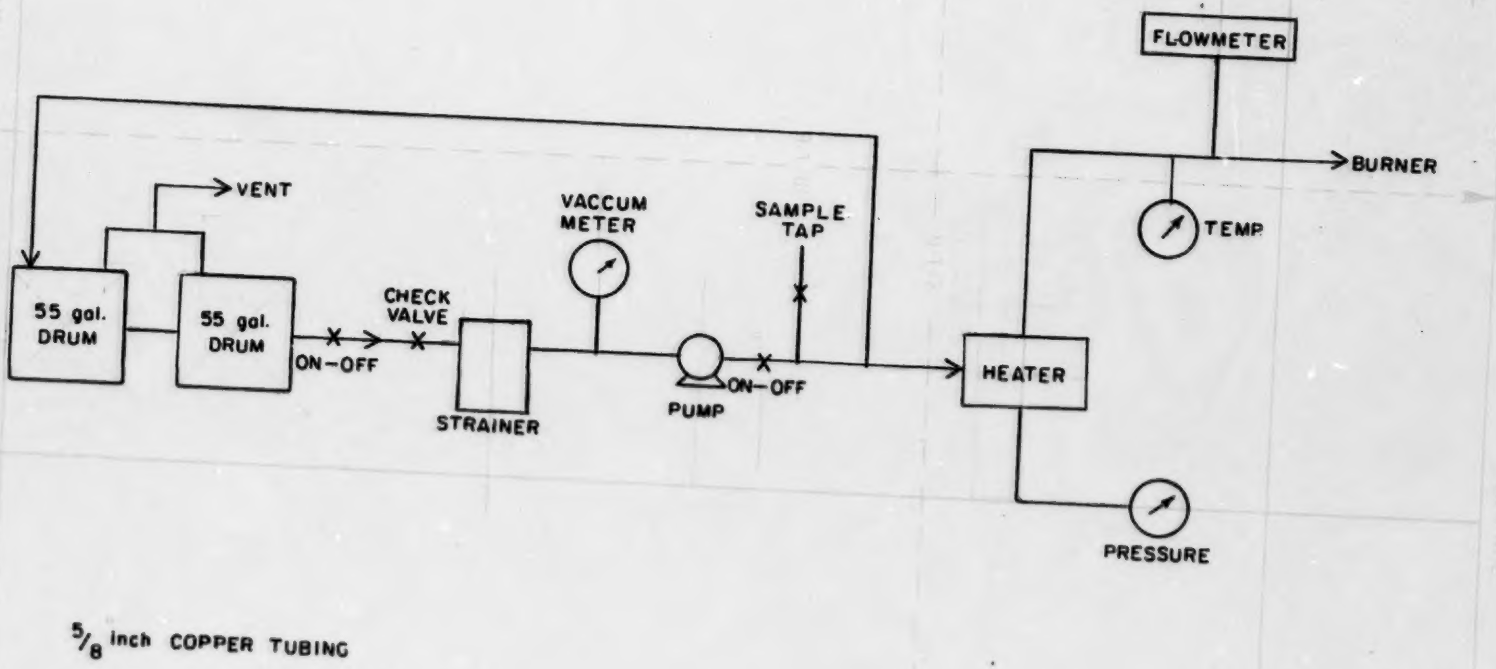

55 gal. DRUM
55 gal. DRUM
VENT
ON-OFF
CHECK VALVE
STRAINER
VACCUM METER
PUMP
ON-OFF
SAMPLE TAP
HEATER
PRESSURE
TEMP
FLOWMETER
BURNER
5/8 inch COPPER TUBING

Figure 8. Fuel Feed System.

FIG. 4-1

## FLUE GAS SAMPLING

The flue gas samples were collected utilizing four principal sampling trains; Modified Method 5, High Capacity Sampling System, Integrated Gas Sampling Train, and Volatile Organic Sampling Train. Each of the individual systems are detailed below.

### Modified Method 5 Train

This train was used to sample simultaneously for particulate, HCl and semivolatile organic species. Isokinetic samples (±10 percent) of the flue gas were collected from the stacks at predetermined sampling points. A schematic of the modified Method 5 train is given in Figure 9.

The sample train consists of a glass-lined heat-traced probe with a stainless steel button hook nozzle and attached thermocouple and pitot tubes. After the probe, the gas passes through a heated glass fiber filter (Reeve Angel 934 AH filter paper). Downstream of the heated filter, the sample gas passes through a water-cooled module, then through a sorbent module that contains a known amount of XAD-2 resin. The XAD module is followed by a series of four impingers. The first impinger, acting as a condensate reservoir connected to the outlet of the XAD module, is modified to have a short stem so that sample gas does not bubble through the collected condensate. The second and third impingers each contain 100 ml of 1N NaOH for HCl collection. The impingers are followed by a pump, dry gas meter, and a calibrated orifice.

### Particle Size Determination

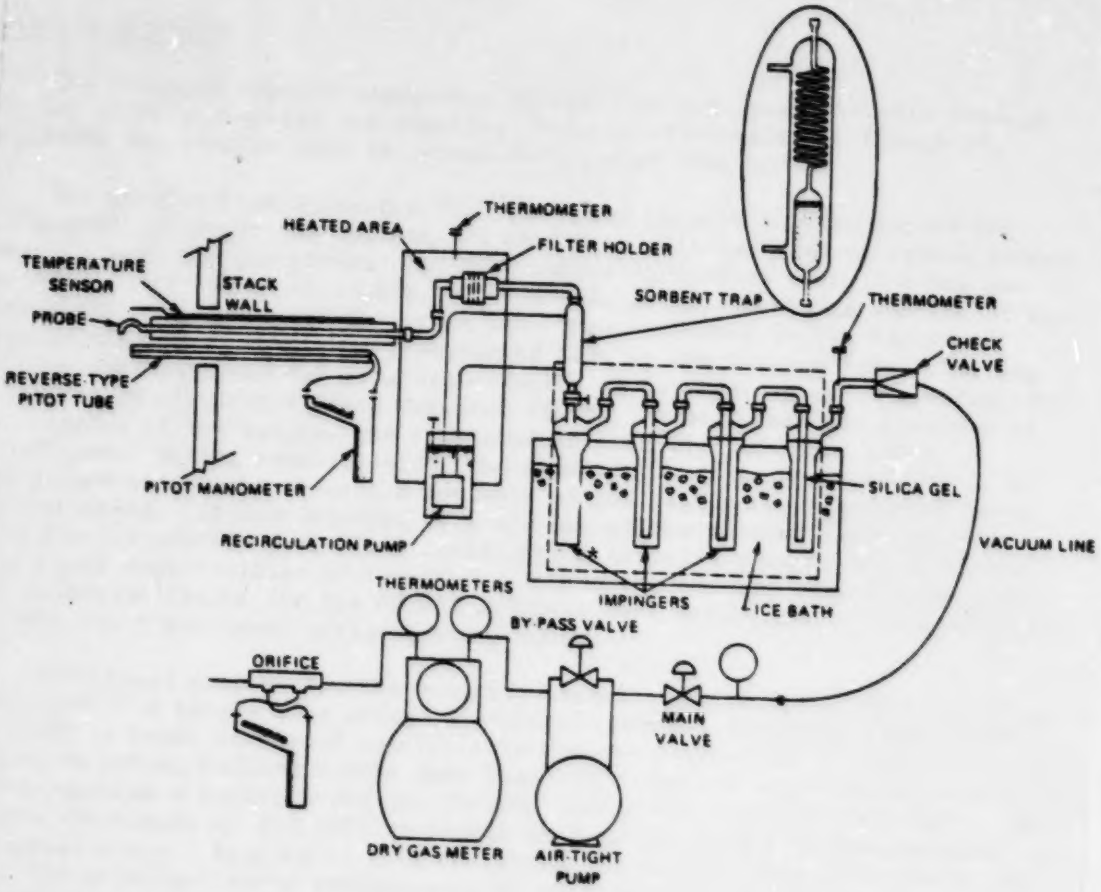
Particle size measurements were conducted at four locations (A, D, E, and G) during the program. The selection of these sites was based on the suitability of the sampling locations at each facility.

These measurements were obtained through the use of an Andersen High Capacity Sampling System (HCSS) Impactor. This method provides for four nominal size cuts: greater than 10 μm, 3-10 μm, 1-3 μm, and less than 1 μm. A representative sample of flue gas was collected from a point of average velocity in the ducts.

In order to obtain an appropriate mass of sample of particulate for lead analysis (100 mg per size cut), the train was operated during each of the test runs at a site but was not recovered until the conclusion of the final run.

### Fixed Gases

An additional integrated gas sample for fixed gases ($O_2$ and $CO_2$) was be collected during each modified Method 5 run. The sample was collected in a Tedlar bag at a rate of 1.0 liter per minute and analyzed for $O_2$ and $CO_2$ with an Fyrite Gas Analyzer in accordance with EPA Method 3.


THERMOMETER
HEATED AREA
FILTER HOLDER
TEMPERATURE SENSOR
STACK WALL
PROBE
SORBENT TRAP
THERMOMETER
CHECK VALVE
REVERSE-TYPE PITOT TUBE
SILICA GEL
PITOT MANOMETER
RECIRCULATION PUMP
VACUUM LINE
THERMOMETERS
IMPINGERS
ICE BATH
BY-PASS VALVE
ORIFICE
MAIN VALVE
DRY GAS METER
AIR-TIGHT PUMP

*First impinger which serves as condensate trap has a very short stem that does not extend into the condensate.

Figure 9. Modified Method 5 train.

The carbon monoxide (CO) content of the flue gas was monitored continuously through the use of a Horiba Model PIR-2000 NDIR instrument, to provide a real time index of combustion efficiency of the unit during the test program.

## Volatile Organics

The volatile organic components of the flue gas were collected through the use of an integrated gas sampling train as illustrated in Figure 10. Duplicate bag samples were collected during each test run.

The samples were extracted from the stack through a probe containing glass wool to remove particulate. A condenser unit was used to remove excess moisture from the gas stream. At the conclusion of each test, the bag was sealed off and stored in opaque containers to prevent photodegradation of the components. The condensate samples were then collected in VOA vials and refrigerated until they were transported back to GCA for analysis. The bag samples were analyzed for volatile organics of interest by gas chromatography utilizing an electron capture detector (ECD). In all cases the analysis of the samples of the samples was completed in less than 48 hours after collection. During initial tests, the remaining samples were removed to a designated clean area where the contents of the bags were purged onto Tenax sorbent resin. It was intended that the use of the sorbent traps in this manner would provide analytical confirmation and also provide for increased analytical sensitivities if required. This technique was discontinued after the detection limits for the GC/ECD analysis were determined to be sufficient to meet the established goals of the program.

Additional samples for the volatile organic components of interest were collected at a single site using the Volatile Organic Sampling Train (VOST). The VOST is being developed specifically for the collection of organic compounds having boiling points less than 100°C and was used intermittently in the program as a backup technique for the Tedlar bag sampling technique. One of the advantages of the VOST technique is that the sample is concentrated on the Tenax resin. Because of this concentration factor, detection limits for both the principal waste contaminants as well as detection limits for potential products of incomplete combustions are enhanced. Use of the VOST train provides a convenient means of scanning for potential by-products of incomplete combustion. The train consists of a glass-lined probe with a glass wool plug to remove particulate, followed by an assembly of condensers and organic resin traps as illustrated in Figure 11. The first condenser cools the gas stream and condenses the water vapor present. The flue gas and condensed moisture then pass through a cartridge containing 1.5 grams of Tenax resin (60-80 mesh). The condensate is collected in the first impinger which is continually purged by the gas stream itself. The second condenser and trap containing Tenax/charcoal (50/50) serve as a backup for low volume breakthrough compounds. Following the second Tenax trap is a series of impingers and drying tubes for residual moisture removal.

The volatile organic samples were collected during the same test period as the modified Method 5 train. The sampling train was operated at a sample flow rate of 0.3 liter per minute for a period of 60 minutes.

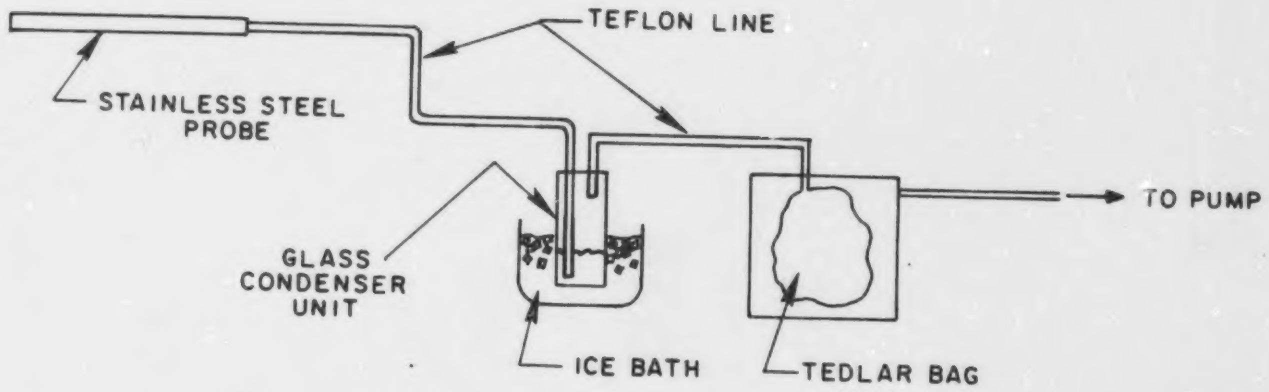

TEFLON LINE
STAINLESS STEEL PROBE
GLASS CONDENSER UNIT
ICE BATH
TEDLAR BAG
TO PUMP

Figure 10. Integrated gas sampling train.

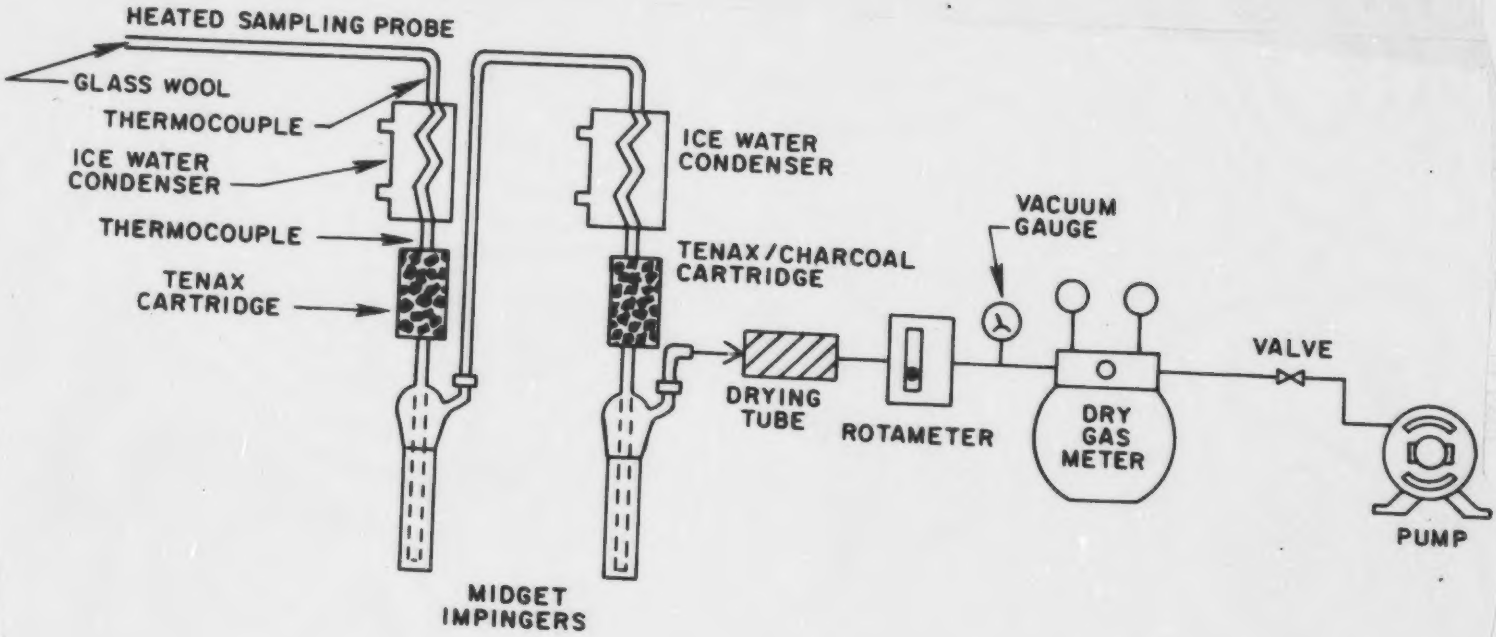

HEATED SAMPLING PROBE
GLASS WOOL
THERMOCOUPLE
ICE WATER CONDENSER
THERMOCOUPLE
TENAX CARTRIDGE
ICE WATER CONDENSER
TENAX/CHARCOAL CARTRIDGE
MIDGET IMPINGERS
DRYING TUBE
ROTAMETER
VACUUM GAUGE
DRY GAS METER
VALVE
PUMP

Figure 11. Schematic of volatile organic sampling train.

# REFERENCES

1. Surprenant, N., et al. The Fate of Hazardous and Non-Hazardous Wastes in Used Oil Disposal and Recycling. DOE/BC/10375. August 1983.

2. EPA Hierachy of Waste Incinerability. Organic Hazardous Constituents Under Incinerator Rules. Released June 21, 1982. Environmental Reporter, June 25, 1982.

# SECTION 5

# ANALYTICAL PROTOCOLS

## INTRODUCTION

As noted previously, samples collected during the test runs performed at six sites were returned to the GCA laboratory for analysis. Samples of fuel feed, flue gas (Tedlar bags and Method 5 train components) and bulk fly ash were submitted for analysis of the components spiked into the fuel feed and of possible combustion by-products. Analyses were performed using GC/MS and/or GC/ECD for volatile and semivolatile organics, ICAP for trace metals and IC for sulfur and chlorine. A detailed discussion of the procedures used for sample preparation and instrumental analysis is presented in subsequent portions of this section.

## SAMPLE BANK/CHAIN OF CUSTODY PROCEDURES

All samples collected over the course of this program were delivered to the GCA Sample Bank at the Bedford facility. Each set of collected samples was accompanied by a sample packing sheet/custody record listing the individual samples by site and field sample code. These records were carefully compared to the submitted sample set to verify sample identification and were then signed by Sample Bank personnel to document the transfer of custody. At the time of receipt, the submitted samples were entered in the Master Log Book where each individual sample was assigned a five-digit GCA Control Number. This unique identification was affixed to the respective sample containers and/or tags and subsequently used throughout all laboratory procedures for positive traceability.

Chain of custody procedures were maintained in the laboratory through the use of GCA Custody Notebooks. At the time of receipt, a page for each sample was entered sequentially by GCA Control Number in the Custody Notebook, and the samples were transferred to the locked Sample Bank refrigerator for storage until the time of analysis. Subsequent handling of the samples was documented by the recording of signatures and dates in the Custody Notebook. In addition, the transfer of samples or extracts between analysts within the laboratory was documented on Sample Custody Transfer forms which become part of the permanent project file and serve as a supplement to the Custody Notebook record of sample handling.

## FUEL FEED ANALYSIS

### Organics

Volatile Organics--

Analysis of fuel feed samples for chloroform, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene was accomplished by extraction followed by purge and trap GC/MS procedures. Sample preparation proceeded as suggested in Method A101b[1] with the substitution of tetraglyme for the polythylene glycol specified. Tetraglyme (tetraethylene glycol dimethyl ether) is similar in chemical and physical properties to polyethylene glycol (suggested in A101b) and is commercially available with fewer interfering contaminants. It has been recommended for extraction of a variety of nonaqueous matrices for volatile organics.[2]

A weighed aliquot (nominally 1 gram) of each fuel feed sample was mixed with 20 ml of precleaned tetraglyme. The sample was shaken until the layers mixed or emulsified (less than 1 minute). The tetraglyme/fuel feed mixture was allowed to equilibrate until phase separation was complete, generally for a period of 12 to 18 hours. The tetraglyme layer was then withdrawn and stored in a screw cap vial with a minimum of headspace at 4°C. Method blanks and quality control spikes were prepared in a similar fashion for all sample sets.

An aliquot of the tetraglyme extract was added to 25 ml "organic free" deionized water for analysis by purge and trap GC/MS techniques. The size of the tetraglyme aliquot was determined by calculating the amount required, based on a given nominal concentration, to produce a concentration of approximately 100 μg/l of the components of interest in the final tetraglyme/water sample. This concentration represents the midpoint of the linear dynamic range of the mass spectrometer.

During this program, tetraglyme volumes spiked into deionized water for analysis ranged from 1 to 20 μl. Each sample was then spiked with bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane internal standards.

Analysis was conducted on a Hewlett-Packard 5985 quadrupole mass spectrometer interfaced to a Tekmar LS3 liquid sample concentrator. Instrumental operating conditions are presented in Table 17 for these analyses. All analyses were performed according to Reference 3 (Method 624) with the following modifications, as routinely implemented at GCA/Technology Division.

- A 25 ml sample was added to the purging chamber with a 30 ml syringe.
- The concentration of internal standard in each sample was reduced by a factor of five in order to prevent detector saturation.
- PFTBA was used for mass spectral tuning in place of PFTPP or BFB.

Standard reference materials of all analytes were used to prepare instrument calibration mixes. Serial dilutions of the components in tetraglyme solution were spiked into deionized water and analyzed to establish

## TABLE 17. GC/MS CONDITIONS FOR VOLATILE ORGANICS ANALYSES

| | |
|---|---|
| **Instrument** | Hewlett-Packard 5985 |
| **GC Conditions** | |
| Column | 1% SP-1000 on Carbopack B, 6 ft x 2 mm ID column |
| Temperature program | 60°C held for 4 min, then 10°/min to 220°C and held |
| Injector temperature | 225°C |
| Carrier flow | UHP helium, 30 ml/min |
| **Purge and Trap Conditions** | |
| Purge gas | UHP helium, 40 ml/min |
| Desorption temperature | 180°C |
| Desorption time | 4 min |
| Oven temperature | 200°C |
| **MS Conditions** | |
| Emission | 300 μa |
| Electron energy | 70 eV |
| Scan rate | 133.3 amu/sec |
| Mass interval | 45-350 amu |

calibration curves for each set of fuel feed samples analyzed. The curves were verified with EMSL standards mixed with tetraglyme on each day of sample analysis. In addition, tetraglyme spiked into deionized water was analyzed daily as a laboratory blank.

Semivolatile Organics--

Submitted samples of composited fuel feed were individually mixed with a pre-rinsed glass rod prior to aliquotting. A 50 mg portion was transferred to a 10 ml volumetric flask and diluted to volume with hexane. An aliquot from this solution was further diluted in hexane to be within the concentration range of calibration standards. Analysis for the components of interest was performed on a gas chromatograph with an electron capture detector (GC/ECD) using the instrument conditions listed in Table 18.

A minimum of four calibration solutions were prepared in hexane and analyzed under the same conditions as program samples. Integrated area responses were plotted versus standard concentration via a linear regression analysis, for which the correlation coefficient always exceeded 0.999.

As mentioned in Section 3, the components spiked into the fuel feed for sites E, F, A and C were 1,2,4-trichlorobenzene, 1-chloronaphthalene and 2,4,5-trichlorophenol. For sites G and D, 2-chlorotoluene was substituted for 2,4,5-trichlorophenol. In preparation for the analysis of samples from sites G and D, calibration standards were generated in order to determine the retention time and response of 2-chlorotoluene relative to the other two components. GC/ECD analysis of calibration standards indicated an absolute detection limit of 100 ng for o-chlorotoluene compared to 40 pg for trichlorobenzene and chloronaphthalene. A second calibration solution was weighed out, diluted and analyzed as a check against preparation error. Similar response was noted for the second solution. A GC/MS analysis of the mixture was then performed, which verified the purity of 2-chlorotoluene. Reference 4 lists similar instances of the effect of aromatic ring substitution on ECD sensitivity.

Because the ECD is more sensitive to trichlorobenzene and chloronaphthalene than chlorotoluene, the presence of the former in the sites G and D fuel feed samples masked the response of chlorotoluene and thus precluded its analysis.

Initial analysis of fuel feed samples from sites E, F, A and C employed silica gel chromatographic cleanup and GC/MS techniques. Analysis of quality control and program samples indicated that the recoveries for trichlorobenzene and trichlorophenol were unusually low, thus necessitating the GC/ECD analysis described above. All reported results are based on GC/ECD data.

## Inorganics

Metals--

The waste oil fuel feed samples were initially prepared for metals analysis by controlled dry ashing. Sample aliquots (2-5 g) in platinum crucibles were placed beneath an array of adjustable heat lamps which were lowered at a rate such that samples neither boiled nor ignited. Samples were exposed for an approximate 8 hr period or until they achieved a tar-like

TABLE 18. GC/ECD CONDITIONS FOR SEMIVOLATILE ORGANIC ANALYSIS OF FUEL FEED

| | |
|---|---|
| Instrument: | Hewlett-Packard 5840A with $Ni^{63}$ electron capture detector |
| Column: | 3 ft x 2 mm (ID) packed with 1% SP 1240 DA on 100/120 mesh Supelcoport |
| Carrier flow: | UHP argon/methane, 35 ml/min |
| Injector temperature: | 300°C |
| Detector temperature: | 350°C |
| Temperature program: (Sites E, F, A, C) | 80°C held for 2 min, then 5°/min to 170°C and held |
| Temperature program: (Sites G, D) | 40°C held for 2 min, then 5°/min to 80°C and held |

appearance. The range of the exposure varied from ambient temperature to approximately 180°C. The samples were subsequently transferred to a cold muffle furnace where the temperature was gradually elevated to 600°C over a period of approximately 6 hr. Each sample was maintained at 600°C until ashing was complete and the resultant ash dissolved by means of 1:1 Ultrex hydrochloric acid. Metals concentrations were subsequently determined via Inductively Coupled Argon Plasma Emission Spectroscopy (ICAP) utilizing a Jarrell Ash Model 855 Atom Comp. The ICAP was calibrated utilizing four working multielement standards prepared to contain 10 mg/l of each element represented on the focal curve. A standard blank (i.e., 2 percent $HNO_3$) was also analyzed. The elements in each individual standard were chosen such that spectrally interfering elements were not combined in any standard mixture.

The model 855 has a background correction system that compensates for continuum background interference. Spectral overlap is compensated for by established interelement correction factors entered into a PDP-8 computer. The PDP-8 minicomputer performs all management functions, data collection, and analysis. Communication with the ICAP is conducted through a Texas Instrument Silent 733 electronic printer. The printer uses cassette magnetic tapes for loading programs and storing data. In addition, the generated data and pertinent sample statistics are fed to another in-house computer, via the Texas Instrument printer, which is programmed to perform all data reduction functions and final data formatting and printing.

Sulfur and Chlorine--

The sulfur and chlorine content of the fuel feed was determined by Parr Bomb combustion followed by Ion Chromatography (IC) analysis. The waste oil fuel feed samples were prepared for sulfur and chlorine analysis by combustion in a bomb containing oxygen under pressure.[5,6] A sample aliquot (0.8 - 1.0 g) was placed in the bomb sample cup over $Na_2CO_3$ absorbing solution. After the assemblage of the bomb, oxygen was slowly admitted to a pressure of 30 atm. The bomb was then immersed in a cold water bath and the electrical circuit completed. Prior to the release of the bomb's internal pressure, it was equilibrated to ambient temperature. The contents were then examined for completeness of combustion. When there was evidence of unburned oil or sooty deposits, the procedure was repeated with a second aliquot. The contents of the bomb and sample cup were copiously rinsed into a beaker where the volume of washings was normally in excess of 300 ml in order to assure complete transfer of the sample. Samples combusted for sulfur analysis were further digested in the presence of bromine water to assure the complete oxidation of all sulfur species to sulfate for subsequent determination by IC. Samples combusted for chlorine analysis were concentrated prior to chloride determination by IC.

The resulting absorbing solutions from Parr Bomb combustions were analyzed for sulfate and chloride by means of a Dionex Model 14 Ion Chromatograph (IC). Sample concentrations were determined by means of standard additions and by comparison of calibration and sample chromatograms. Working standards for sulfate (5 to 40 ppm) and chloride (1 to 20 ppm) were prepared daily from their respective 1000 ppm stock solutions utilizing deionized water as a diluent. Table 19 presents the operating conditions of the IC for both sulfate and chloride analysis.

TABLE 19. INSTRUMENT OPERATING PARAMETERS FOR IC ANALYSIS

| | |
|---|---|
| Instrument: | Dionex Model 14 Ion Chromatograph (IC) |
| Columns: | Anion precolumn, anion separator column, fiber suppressor column |
| Injection Loop: | 100 µl |
| Eluent: | 0.003 M Na $HCO_3$/0.0024 M $Na_2CO_3$ |
| Suppressor Regenerating Solution: | 0.025 N $H_2SO_4$ |
| Flow Rate: | 138 ml/hr |

Those samples exhibiting a matrix interference for chloride on the IC were quantified utilizing a Technicon Auto Analyzer II according to the protocol specified in Method 325.2.[7] This automated, colorimetric procedure involves the addition of mercuric, thiocyanate and ferric nitrate solutions to both standards and samples followed by an absorbance measurement, at a wavelength of 480 nm. Working standards in the range of 1 to 30 mg/l were prepared daily from a 1000 mg/l chloride stock solution. Sample concentrations were determined by comparison of sample percent scale to the established standard curve.

Physical Properties--

The physical properties of the fuel feed were determined by Gilbert Associates in Reading, PA. As indicated in Table 20, the parameters of interest were measured using standard ASTM procedures.

TABLE 20. ANALYSES FOR PHYSICAL CHARACTERIZATIONS OF OILS

| Analysis | ASTM method |
|---|---|
| Ultimate analysis | D3178 |
| API gravity | D287 |
| Pourpoint | D90 |
| Flashpoint | D93 |
| Viscosity | D445 |
| Water by distillation | D86 |
| Chlorine | D808 |
| Sulfated ash | D874 |
| Higher heating value | D240 |
| Density | D1298 |
| Copper corrosion test | D130 |
| Sediment | D473 |

## FLUE GAS

### Organics

#### Volatile Organics--

GC/ECD analysis--Flue gas samples were collected in 25 liter Tedlar bags which were then placed inside black plastic bags for transport to the GCA laboratory at the completion of each day's testing. Coordination of field and laboratory schedules ensured the start of analysis with a minimum of delay after sample receipt. In all cases, analysis was complete within 48 hours of sampling.

Analysis for chloroform, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene was performed using a gas chromatograph with an electron capture detector (GC/ECD) under the operating conditions listed in Table 21. Each Tedlar bag was connected through the gas sampling valve to a Dupont P125 pump (via Teflon tubing). Sample gas was aspirated from each bag through the loop for a period of 30 seconds. The sample was then injected onto the GC by diverting carrier flow through the sample loop. Each Tedlar bag was analyzed in duplicate with ±10 percent replication as criterion for acceptance.

Calibration standards were prepared by injecting microliter quantities of commercially available solvents into a Supelco 500 ml gas sampling bulb which had been previously rinsed with hexane, heated at 120°C and prepurged with nitrogen. Serial dilutions were then performed using a gas-tight syringe in several 1-liter prepurged Tedlar bags in order to provide a four-point calibration curve between 40 and 1500 $\mu g/m^3$. Calibration standards were analyzed under the same operating conditions as samples. A minimum of two of the four calibration points was analyzed in duplicate with an acceptance criterion of ±10 percent. Calibration curves were prepared from a linear regression analysis of the integrated area response from the injections of calibration standards. Calibration curves were rejected if the correlation coefficient of the linear regression analysis was less than 0.99. All samples were quantified by entering the sample area response into the appropriate calibration curve. Reported results represent the mean of two determinations.

The accuracy of the calibration standards was periodically checked against gas standards generated from VICI/Metronics Dynacal® permeation tubes, certified against NBS traceable standards. Dilution gas flow rate and permeation temperature were controlled by a VICI/Metronics Model 340 Dynacalibrator™.

Samples from sites E and F were initially analyzed on a Hewlett-Packard 5840A GC/ECD using a Hamilton 1001-LT 1.0 ml gas-tight syringe for sample injection. Standards for calibration were prepared in the manner mentioned above, but also injected via syringe. The analysis of standards showed the same linearity and reproducibility found later with loop injections. However, it was found that after the analysis of several flue gas samples, either the syringe or the injector had altered such that the response to standards was no longer linear or reproducible. In addition, the analysis of blanks indicated a carryover problem, especially evident with tetrachloroethylene. Corrective

TABLE 21. GC/ECD CONDITIONS FOR TEDLAR BAG ANALYSIS

| | |
|---|---|
| Instrument | Perkin Elmer 3920 with $Ni^{63}$ electron capture detector and Spectra Physics Minigrator |
| GC Condtions | |
| Column | 20% SP 2100/0.1% Carbopack 1500 on 100/120 mesh Supelcoport, 10 ft x 1/8 in. SS column |
| Temperature | Isothermal at 50°C |
| Injector temperature | 110°C |
| ECD temperature | 325°C |
| Carrier flow | 25 ml, argon/methane |
| Sampling Valve Conditions | |
| Loop volume | 1 ml |
| Loop temperature | 125°C |

measures such as syringe replacement, heating and purging the syringe between injections, rinsing the syringe with solvents and increasing the injection temperature could not be relied upon to provide permanent relief from these problems. As a result of the above difficulties, valid data on the bag samples could not be generated within the 48-hour holding time and sampling for those two sites was rescheduled for a later date. In the interim, a Perkin-Elmer 3920 with a heated gas-sampling valve was substituted for these analyses.

Tenax tube analysis--Aliquots of selected Tedlar bag samples, collected during this program, were drawn over Tenax-packed adsorbent tubes for analysis by thermal desorption--GC/MS. The primary purpose for this analysis was qualitative confirmation of the major volatile components measured by GC/ECD.

All Tenax used in this program was subjected to a preparative cleanup procedure, which included sequential soxhlet extraction (16-hour each) with methanol and pentane and a 2-hour drying period, 8 to 10 inches from a heat lamp. The glass tubes and culture tubes were washed with soap and water, rinsed with deionized water, and baked at 105°C overnight. Glass wool to be used to secure the Tenax in place was soxhlet-extracted with pentane, and oven-dried at 105°C overnight. Each tube was packed with 1.2 ± 0.05g of Tenax and then conditioned for sampling for two 2-hour periods by heating to 250°C under a helium purge flow of approximately 15 cc/min.

Once GC/ECD analysis of the selected bag samples had been completed, the volume of gas to be drawn over Tenax was calculated using the concentrations measured by GC/ECD. This calculation determined the volume required to provide sufficient quantities of the components of interest without saturating the mass spectrometer. Sample gas from Tedlar bags was then drawn over Tenax using Dupont P-4000 pumps.

Exposed Tenax cartridges were introduced to the mass spectrometer via a three step process. The components of interest were first desorbed into a capillary trap cooled with liquid nitrogen. This desorption was accomplished using a Nutech Model 320 Thermal Desorption Unit under the conditions specified in Table 22. The capillary trap was then heated to 210°C to vaporize the condensed components onto the head of the GC column. This vaporization required rapid heating of the capillary trap in order to limit band-broadening. As a further deterrent to band-broadening, the head of the GC column was cooled by a spray of liquid nitrogen for 2 minutes during sample introduction. Additional instrumental conditions are provided in Table 22.

Calibration for the compounds of interest was achieved by injection, via gas-tight syringe, of varying amounts of a vapor phase stock standard onto blank Tenax tubes under negative pressure. Vapor phase stock standards were prepared by injecting a known volume of a standard mixture into a 250 ml sampling bulb and allowing the bulb to equilibrate in a 35°C water bath. A minimum of five calibration standards were analyzed on each day of analysis. Linear regression plots of total nanograms per tube versus response were made to calculate sample concentrations.

TABLE 22. THERMAL DESORPTION GC/MS--INSTRUMENT OPERATING CONDITIONS

| | |
|---|---|
| Thermal Desorption Conditions | |
| Instrument | Nutech Model 320 |
| Cartridge desorption temperature | 250°C |
| Cartridge desorption time | 10 minutes |
| Desorption flow rate | 11 cc/min |
| Capillary trap temperature | -196°C (mininum), 210°C (maximum) |
| GC/MS Conditions | |
| Instrument | Hewlett-Packard 5993 GC/MS/DS |
| GC Conditions | |
| Column | 50 meter SE 30 glass capillary column |
| Temperature program | 70°C held for 4 minutes, then 4°/minute to 120°C and held |
| Injector temperature | 225°C |
| Carrier flow | UHP helium, 2 ml/min |
| MS Conditions | |
| Emission | 300 μa |
| Ionization energy | 70 eV |
| Scan rate | 1 sec/scan |
| Mass range | 41-350 amu |

Additionally, at least two cartridges spiked with an independently prepared reference standard were run on each day of analysis. These cartridges were spiked with the components of interest at equivalent concentrations in order to build a data base.

As standard operating procedures in the GCA laboratory, the HP 5993 GC/MS is tuned daily to criteria established for PFTBA rather than for BFB as specified in EPA Method 624.[3] PFTBA was continuously bled into the source during adjustment of instrument parameters in order to meet the following ion abundances:

| Mass | Ion Abundance Criteria |
|---|---|
| 69 | 100 percent |
| 131 | 25 to 30 percent of mass 69 |
| 219 | 20 to 25 percent of mass 69 |

VOST analysis--As previously mentioned, additional sampling using the VOST train was performed for volatile organics at site D. The Tenax and Tenax/charcoal samples generated from the VOST train were analyzed by thermal desorption GC/MS procedures for volatile organic compounds.

Thermal desorption of samples was conducted in a Nutech Model 320 apparatus maintained at 250°C for all Tenax samples. Equipment failure during Tenax/charcoal sample analysis necessitated the use of heating tape for desorption in place of the Nutech unit for the remaining program samples. Standards and blanks run at the time of this substitution verified its equivalency.

Flow from the desorption unit was directed through 3 ml deionized water in the purge chamber of a Spex/Chromalytics purge and trap sample concentrator. To minimize the volume of water entering the adsorbent trap of the concentrator, the purging chamber was cooled in an ice/water bath during sample desorption. At the midpoint of the desorption period, 300 ng of $d_6$-benzene and $d_8$-toluene were injected directly onto the adsorbent trap to serve as internal standards for the subsequent GC/MS analysis.

Analyses were conducted on a Hewlett-Packard 5993 quadrupole mass spectrometer. Instrumental operating conditions for these analyses were as shown in Table 23. Instrument tuning and calibration for the four chlorinated volatile organics (chloroform, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene) were accomplished as outlined above for previous Tenax analyses. Method blanks and single point calibration checks were analyzed at 4-hour intervals during sample analysis.

Additionally, volatile organics other than the four components of interest were identified in each sample employing a forward search of the EPA/NIH mass spectral library. Only the spectra of those components present at levels greater than those of the internal standards were selected. Where necessary, background correction of the mass spectrum was achieved by computer subtraction. A probability-based library search (PBS) was then conducted by

TABLE 23. GC/MS INSTRUMENT OPERATING CONDITIONS FOR VOST ANALYSIS

| | |
|---|---|
| Thermal Desorption Conditions | |
| Instrument | Nutech Model 320 |
| Cartridge desorption temperature | 250°C |
| Cartridge desorption time | 10 minutes |
| Desorption flow rate | 40 cc/min |
| GC/MS Conditions | |
| Instrument | Hewlett-Packard 5993 equipped with a Spex/Chromalytics purge and trap device |
| Trap Packing | Tenax (60/80 mesh), 3% OV-1 on Chromosorb W (60/80 mesh), silica gel (Davison grade 15, 35/60 mesh) |
| Purge and Trap Conditions | |
| Desorption temperature | 180°C |
| Desorption time | 4 min |
| GC Conditions | |
| Column | 1% SP-1000 on Carbopack B, 6 ft x 2 mm ID column |
| Temperature program | 80°C held for 4 min, then 10°/min to 200°C and held |
| Injector temperature | 225°C |
| Carrier flow | UHP helium, 30 ml/min |
| MS Conditions | |
| Emission | 300 μa |
| Ionization energy | 70 eV |
| Scan rate | 133.3 amu/sec |
| Mass interval | 41-350 amu |

computer routine, comparing the unknown spectra with those of the EPA/NIH libraries. The computer search provided up to 10 possible matches; positive identification was made by the analyst when the following conditions were met:

- The intensity, relative to the base peak, of all major peaks (greater than 30 percent of the base peak) agreed within 20 percent.
- All peaks present in the library spectrum at greater than 20 percent of the base peak were present in the unknown spectrum.
- The unknown spectrum did not have any peaks present at greater than 20 percent of the base peak that were not in the library spectrum or were not clearly attributable to coeluting material.

Concentrations of identified components were calculated relative to the closest eluting internal standard. Area count response for the total ion peak of the unknown was compared to that for the internal standard. In cases were interference from coeluting material made this method unreliable, extracted ion areas for the base peaks of the unknown and internal standard were compared. The majority of additional components identified were hydrocarbons with molecular weights ranging from 78 to 98. It should be noted that benzene and toluene, also found in several samples, are possibly derived as sorbent contaminants and are known products of Tenax thermal degradation.[8] In all cases, the reported values for these compounds were corrected by the appropriate method blank.

Condensates collected with the VOST samples were analyzed for the four chlorinated organic solvents spiked into the fuel feed. Analysis was performed by purge and trap GC/MS techniques as outlined in EPA Method 624.[3] Modifications to this protocol as implemented in the GCA laboratory include the following:

- A 25 ml sample was added to the purging chamber with a 30 ml syringe. This change from the recommended 5 ml sample allowed a fivefold increase in sensitivity to be achieved (0.5 to 1.0 ppb).
- The concentration of internal standard in each sample was reduced by a factor of five in order to prevent detector saturation.
- PFTBA was used for mass spectral tuning in place of PFTPP or BFB.

### Semivolatile Organics--

As previously mentioned, sampling for semivolatile organic components in the flue gas stream was accomplished via Method 5 particulate train. Each train produced the following types of sample: particulate collected on a filter, solvent probe rinse, XAD-2 sorbent and condensate/impingers.

Particulate filters and probe rinses were equilibrated and weighed to constant weight (±0.5 mg). Once particulate weights had been recorded, the filter and probe rinse were transferred to a soxhlet extraction apparatus along with the appropriate XAD sample. The combined sample was then surrogate-spiked with approximately 200 µg each of $d_5$-phenol, $d_3$-trichlorobenzene, $d_{10}$-biphenyl and $d_{12}$-chrysene, and soxhlet-extracted overnight with 700 ml methylene chloride. The solvent extract was held for combination with the impingers extract.

The impinger waters were transferred to a separatory funnel along with a methylene chloride rinse of the sample containers. The sample was then extracted three times with methylene chloride and the extracts combined with the appropriate XAD extract and train rinse. This combined extract was dried with anhydrous sodium sulfate and concentrated to less than 2.0 ml with a Kuderna-Danish evaporator. The final volume was adjusted to 2.0 ml with methylene chloride.

A 1.0 ml portion of the 2.0 ml extract was analyzed with the mass spectrometer operating in the continuous scanning mode to provide the identification and quantitation of a wide variety of semivolatile components. The second portion was reserved for further volume reduction and GC/MS analysis in the selected ion monitoring (SIM) mode to provide detection of targeted dibenzofurans and dibenzo-p-dioxins with enhanced limits of sensitivity.

Comprehensive analysis--The 1.0 ml aliquot for comprehensive semivolatile analysis was spiked with 20 µg each of $d_8$-naphthalene and $d_{10}$-anthracene to serve as internal standards. Analysis was performed on an HP 5985 GC/MS quadrupole mass spectrometer in accordance with the EPA Method 625[3] requirements for mass spectral analyses. Table 24 lists the operating parameters used for this portion of the program. Standard operating procedure in the GCA laboratories required tuning with PFTBA in place of the DFTPP listed in Method 625.

Extracted ion profiles were obtained for the primary ions of the semivolatile components spiked into the fuel feed (2,4,5-trichlorophenol, 1,2,4-trichlorobenzene and **1-chloronaphthalene** for Sites E, F, A, C and 2-chlorotoluene, 1,2,4-trichlorobenzene and **1-chloronaphthalene** for Sites G and D). Identification and quantitation of these components was consistent with the criteria of Method 625 and was based on data collected for three concentration levels of reference standards analyzed prior to sample analyses for each site.

Additional components in the sample were identified through computerized library search routines. Background-corrected spectra were obtained for major peaks noted in the total ion chromatograms, with special attention focused on all peaks with fragmentation patterns characteristic of halogenated compounds. Forward searches of the NIH/EPA library files yielded up to 10 possible matches for each unknown spectra. Positive identifications were assigned to those meeting the criteria outlined for the identification of additional components for VOST samples.

It should be noted that a number of the components frequently identified in the Method 5 train flue gas can occur as contamination arising from the XAD-2 polymeric sorbent material, or as artifacts formed by exposure of the

TABLE 24. GC/MS OPERATING CONDITIONS FOR SEMIVOLATILE COMPREHENSIVE ANALYSIS

| | |
|---|---|
| Instrument | Hewlett-Packard 5985, quadrupole mass spectrometer |
| GC Conditions | |
| Column | SE 54 30m fused silica capillary |
| Temperature program | 50°C held for 2 min then 10°/min to 260°C and held |
| Injector type | Grob w/0.5 min sweep time |
| Injector temperature | 275°C |
| Injection volume | 1 µl, splitless |
| Column flow | UHP helium, 0.5 ml/min |
| MS Conditions | |
| Emission | 300 µa |
| Electron energy | 70 eV |
| Scan time | 1.0 sec/scan |
| Mass interval | 45 to 400 amu |
| Source temperature | 200°C |

XAD-2 resin to actual combustion source flue gases.[8-11] It is our opinion, however, that since the XAD-2 sorbent was subjected to rigorous clean-up and quality control prior to use in the field that these components are primarily attributable to the flue gas samples, themselves, and are not sorbent artifacts. This is further supported by the appearance of some of the same components on bulk particulate samples, as well, which are not impacted by the sorbent collection system in the flue gas. It should be further noted that data reported for these components in actual samples represent blank corrected values. (The majority of these compounds were not in evidence in either method blanks or the field-biased blanks which accompanied samples during field sampling operations, transport and storage.)

In addition, a number of sample extracts contained high levels of phthalates, which are commonly used plasticizers and frequent contaminants in samples subjected to extensive laboratory handling.[12] Also present in some samples were high molecular weight aliphatic compounds. Because fragmentation patterns for homologues are identical, and retention times from standard reference materials were unavailable, the mass spectral data collected from electron impact ionization of these samples did not provide sufficient information for component identifications. As a result, the high molecular weight aliphatics noted could not be identified and reported.

Several samples contained semivolatile compounds included on the EPA list of Priority Pollutants. These were quantitated using response factors generated for standards analyzed prior to sample analyses. Additional components were quantitated through a comparison of their total ion peak areas with that for the closest-eluting internal standard.

Dioxin/dibenzofuran analysis--The Method 5 train sample aliquots reserved for SIM analysis were concentrated to 100 µl by nitrogen blowdown prior to analysis. These were then spiked with 2 µg $d_{12}$-anthracene as an internal standard.

Calibration mixtures of dibenzo-p-dioxins and dibenzofurans as listed in Table 25 were prepared using standard reference materials obtained from Ultra Scientific, Hope, R.I. GC/MS analyses of the mixtures were initially conducted in the continuous scanning mode to establish appropriate chromatographic conditions and to determine characteristic ions to monitor for each compound class.

Analyses were conducted on the Hewlett Packard 5985 GC/MS. Instrument tuning was adjusted to allow maximum sensitivity for high molecular mass ions. Tuning criteria for PFTBA during these analyses were as follows:

| Mass | Ion Abundance Criteria |
|---|---|
| 69 | base peak, 100% |
| 219 | 45-55% |
| 502 | 1.5-2.5% |

Instrument operating parameters for the SIM analyses are presented in Table 26. Retention time windows established for the classes of targeted compounds and ions monitored within these windows are shown in Table 27. In

TABLE 25. SUMMARY LISTING OF DIBENZOFURAN AND DIBENZO-P-DIOXIN REFERENCE MATERIAL

Dibenzofuran

Dibenzo-p-dioxin

1-Chlorodibenzo-p-dioxin

2-Chlorodibenzo-p-dioxin

2,3-Dichlorodibenzo-p-dioxin

2,7-Dichlorodibenzo-p-dioxin

1,2,4-Trichlorodibenzo-p-dioxin

1,2,3,4-Tetrachlorodibenzo-p-dioxin

1,2,3,7,8-Pentachlorodibenzo-p-dioxin

1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin

Heptachlorodibenzo-p-dioxin

Octachlorodibenzo-p-dioxin

2,7-Dichlorodibenzofuran

Octachlorodibenzofuran

TABLE 26. GC/MS OPERATING CONDITIONS FOR SELECTED ION MONITORING

| | |
|---|---|
| Instrument | Hewlett-Packard 5985, Quadrupole Mass Spectrometer |
| GC Conditions | |
| Column | SE-54 30m fused silica capillary |
| Temperature program | 60°C held for 1 min then 12/min to 260°C and held |
| Injector type | Grob with 0.5 min sweep time |
| Injector temperature | 275°C |
| Injection volume | 1 μl, splitless |
| Column flow | UHP helium, 0.5 ml/min |
| MS Conditions | |
| Emission | 300 μa |
| Electron energy | 70 eV |
| Source temperature | 200°C |

TABLE 27. GC/MS SIM ANALYSIS FOR DIBENZOFURANS AND DIBENZO-P-DIOXINS - COMPONENT IDENTIFICATION CRITERIA

| Retention time window | Isomer class | Ions monitored | | | Mass dwell time (milliseconds) |
|---|---|---|---|---|---|
| 10.0 - 15.0 minutes | Dibenzofuran | 168 | 139 | | 100 |
| | Dibenzo-p-dioxin | 184 | 128 | | 100 |
| | Chlorodibenzofurans | 202 | 204 | | 100 |
| | Chlorodibenzo-p-dioxins | 218 | 220 | 155 | 100 |
| 15.0 - 18.0 minutes | Dichlorodibenzofurans | 236 | 238 | | 100 |
| | Dichlorodibenzo-p-dioxins | 252 | 254 | 189 | 100 |
| | Trichlorodibenzofurans | 270 | 272 | | 100 |
| | Trichlorodibenzo-p-dioxins | 288 | 290 | 218 | 100 |
| 18.0 - 23.0 | Tetrachlorodibenzofurans | 304 | 306 | 308 | 80 |
| | Tetrachlorodibenzo-p-dioxins | 320 | 322 | 257 | 80 |
| | Pentachlorodibenzofurans | 338 | 340 | 342 | 80 |
| | Pentachlorodibenzo-p-dioxins | 356 | 358 | 293 | 80 |
| 23.0 - 32.0 | Hexachlorodibenzofurans | 372 | 374 | | 100 |
| | Hexachlorodibenzo-p-dioxins | 388 | 390 | | 100 |
| | Heptachlorodibenzofurans | 406 | 408 | 410 | 100 |
| | Heptachlorodibenzo-p-dioxins | 424 | 426 | | 100 |
| 32.0 - 40.0 | Octachlorodibenzofuran | 440 | 442 | 444 | 160 |
| | Octachlorodibenzo-p-dioxin | 458 | 460 | 462 | 160 |

the course of analysis of program samples, replacement of the fused silica capillary column altered retention times and the SIM program was adjusted accordingly.

Serial dilutions of standard mixes were analyzed to determine average relative response factors for the SIM analyses. Single-point calibration checks were run on each day of analysis.

Criteria for component identification required that the monitored ions for a particular group of isomers maximize within one scan and elute within ±1.5 minutes of the standard reference material for that class of compound. In addition, relative ion intensities for the monitored ions were expected to be within ±20 percent of those noted for the standard reference material. For those chlorinated dibenzofurans for which isomer reference materials were not available, expected retention times and ion intensities were based upon those noted for the corresponding dibenzo-p-dioxin standard.

Two samples, Run 2 at Site F and Run 4 at Site C, did not concentrate to 100 μl during the nitrogen blowdown step. These samples were subjected to the alumina column chromatography procedure detailed in Method 613.[3] Quality control samples, prepared and analyzed with the program samples, indicated significant losses of dibenzofuran, monochloro- and octochloro-isomers. Recovery of dichloro-isomers was satisfactory. (See Section 6.) Consequently, the reported results for dioxin/furan analysis of these samples represent minimum values. Three additional samples, Run 1 at Site F, Run 4 at Site A and Run 3 at Site C, were subjected to alumina cleanup after initial SIM analysis indicated interferences with dioxin/furan identifications. For these samples, quantitation of identified dioxin/furan components was based on the pre-alumina analysis. The second analysis was used only to confirm the presence of each component class.

## Inorganics

### Trace Metals--

Particulate filters and probe rinses from Method 5 trains were also prepared for trace metals analysis. Sample aliquots (0.8-1.0 g) were initially digested in 3M nitric acid. The digestates were then filtered through a 0.45 μm Millipore filtering apparatus. The filter plus the insoluble particulates were subsequently digested with hydrofluoric acid in order to achieve total dissolution of silicate material in the fly ash. The resulting digestate as well as the 3M nitric filtrate were then analyzed for metals by means of Inductively Coupled Argon Plasma Emission Spectroscopy (ICAP) utilizing a Jarrell Ash Model 855 Atom Comp. The instrument operating conditions and standards preparation were the same as those previously described for metals analysis of fuel feed samples.

The size distribution of particulate lead was measured using an Andersen High Capacity Sampling System (HCSS) Impactor, which generated five samples for lead analysis: a thimble and cuts of 10 μm, 3-10 μm, 1-3 μm and <1 μm (filter rinse). The thimble portion of the HCSS Impactor was prepared for lead analysis according to the procedures described in Appendix D of

Reference 1, modified to employ the use of 3M nitric acid as the extractant in lieu of aqua regia. The filter rinse, 1 μm, 3 μm, and 10 μm particulates were prepared for lead analysis according to the protocol discussed previously for the particulate analysis. Lead concentrations were quantified by means of Inductively Coupled Argon Plasma Emission Spectroscopy (ICAP) utilizing a Jarrell Ash Model 855 Atom Comp.

Lead concentrations on those samples exhibiting a matrix interference were measured by Atomic Absorption Spectrophotometry (AAS) utilizing a Varian Model AA6 AAS.

Chloride--

Chloride analysis of the impinger solutions was accomplished by direct injection of each sample into a Dionex Model 14 Ion Chromatograph (IC). Instrument operating conditions and standards preparation have been previously described for chloride and sulfate analysis of fuel feed samples.

Sample interferences were overcome via analysis by automated colorimetry. This technique was previously described in the discussion of chloride and sulfate analysis of fuel feed samples.

## FLY ASH

### Organics

Semivolatile Organics--

Four 200g samples of boiler ash were prepared for semivolatile organics analysis. The samples were surrogate-spiked with $d_5$-phenol, $d_5$-trichlorobenzene, $d_{10}$-biphenyl and $d_{12}$-chrysene and soxhlet-extracted for 24 hours in methylene chloride. The extract was then concentrated via Kuderna-Danish to the minimum volume possible. Due to significant quantities of high boiling organics, the final volume was 3.0 or 4.0 ml rather than the 2.0 ml suggested in the test plan. A 1.0 ml volume of this extract was then spiked with $d_8$-naphthalene and $d_{10}$-anthracene to serve as internal standards and analyzed by GC/MS. Instrumental conditions and operating parameters used for these analyses are summarized in Table 24. The high organic content of the first fly ash extracts analyzed resulted in instrumental saturation; the remaining two and WO-D-FA-3 and WO-D-FA-4 were diluted by a factor of 10 prior to analysis. Two of the three spiked semivolatile components, 1,2,3-trichlorobenzene and 1-chloronaphthalene, were identified and quantitated as in the Method 5 train extract samples. Because of its greater volatility, 2-chlorotoluene was not expected to be present in the fly ash. The identification of additional components in these samples was complicated by the high organic levels and the complexity of the organic content. Chromatographic resolution of the sample extracts was incomplete; coeluting homologues of aliphatic hydrocarbons and alkyl-substituted aromatic hydrocarbons made individual peak determinations possible only for major components. These were primarily aromatic hydrocarbons and related oxygenated species, with some aromatic nitrogen and sulfur compounds present as well.

An additional 1 ml aliquot of each fly ash extract was then subjected to alumina column chromatography and concentration to 100 μl as previously described for flue gas (Method 5 train) analysis. A discussion of the problems encountered with this cleanup technique was described for flue gas. The samples were analyzed by selected ion monitoring (SIM) GC/MS for dibenzo-p-dioxins and dibenzofurans. Analysis conditions and instrumental parameters were as given in Table 26.

Measurable levels of polychlorinated dibenzodioxins and dibenzofurans were detected in the fly ash samples. One concentrated extract, that of WO-D-FA-3, was selected for analysis in the total ion mode to confirm the presence of these species. Figure 12 presents the total ion chromatogram for this analysis. Figure 12 demonstrates that alumina column chromatography did not completely remove the complex organic matrix of the sample; high levels of polynuclear aromatic compounds were noted in conjunction with a wide variety of chlorinated species. Complete mass spectra were obtained for peaks identified by SIM as hexachloro-, heptachloro-, and octachlorodibenzo-p-dioxins. The molecular ion isotope abundances of these isomers matched those of the standard reference materials of these isomer classes. Additionally, major fragmentation ions seen in spectra of the standards were present in sample spectra. Mass spectra for the peaks identified as chlorinated dibenzofurans were also obtained. Spectra in all cases displayed the expected isotope abundances for the molecular ion of the identified isomer class. Figures 13 and 14 illustrate the characteristic isotopic abundance ratios noted for the molecular ion of the standard pentachlorodibenzo-p-dioxin (MW = 354 amu) and that observed for the corresponding pentachlorodibenzofuran (MW = 338 amu) identified in the fly ash extract.

Dioxin/furan results of fly ash analyses were compared with those obtained from the analyses of Method 5 trains at Site D. The comparison indicated that the levels measured in bulk fly ash would not have been detectable in the small quantity of particulate collected by the Method 5 train.

### Trace Metals--

Submitted fly ash samples were prepared for metals analysis via extraction with hot 3M nitric acid. Sample aliquots (0.3-0.5g) were extracted for a period of 1 hour and the generated leachate subsequently filtered through a Whatman No. 42 filter. Metals determination of the resultant filtrate was accomplished by Inductively Coupled Argon Plasma Emission Spectroscopy (ICAP) utilizing a Jarrell Ash Model 855 Atom Comp. The instrument operating conditions and standards preparation procedures have been previously described for metals analysis of fuel feed samples.

### Chloride--

Fly ash samples were prepared for chloride analysis by means of a hot water extraction. Sample aliquots (0.8-1g) were heated with deionized water for a period of 30 minutes. The solutions were then filtered and the resulting filtrates subsequently analyzed for chloride utilizing a Dionex Model 14 Ion Chromatograph (IC). Instrument operating conditions and standards preparation have been previously discussed for fuel feed samples.

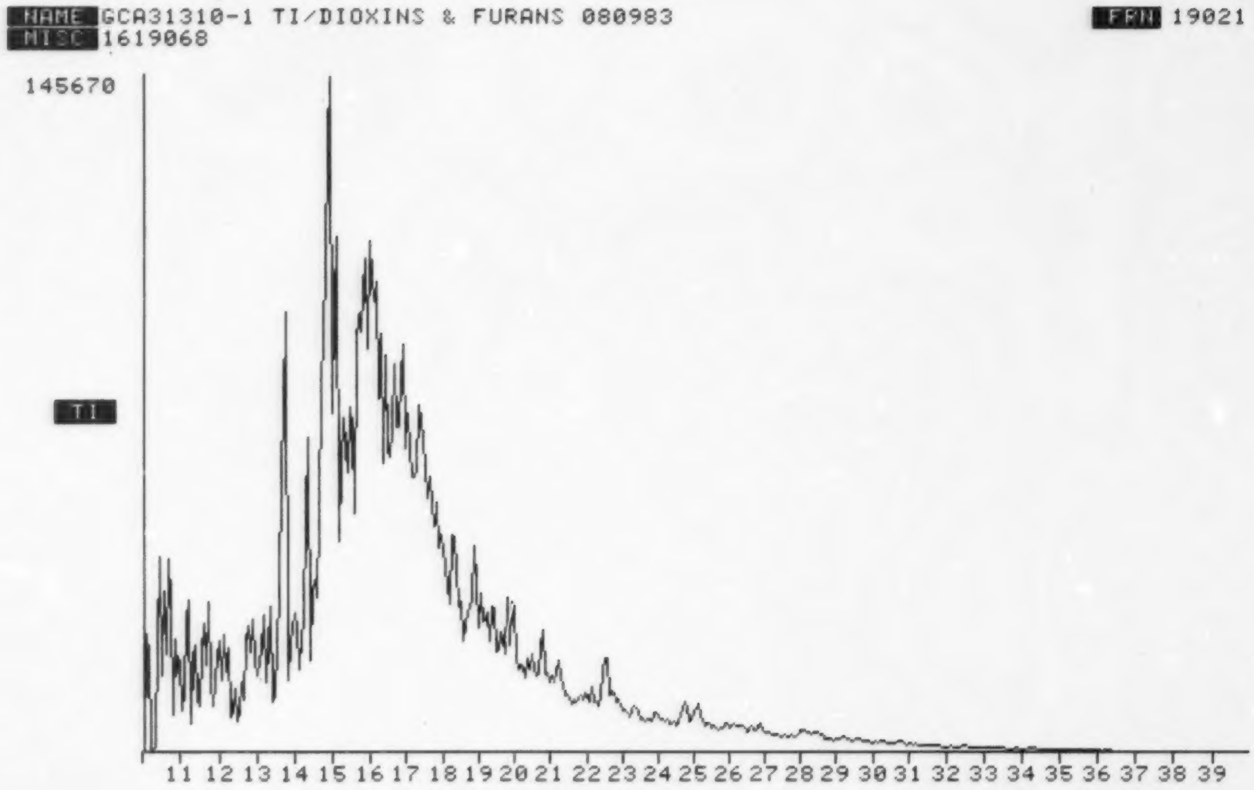


Figure 12. Total ion chromatogram of fly ash extract cleaned by alumina chromatography.

Reproduced from best available copy.

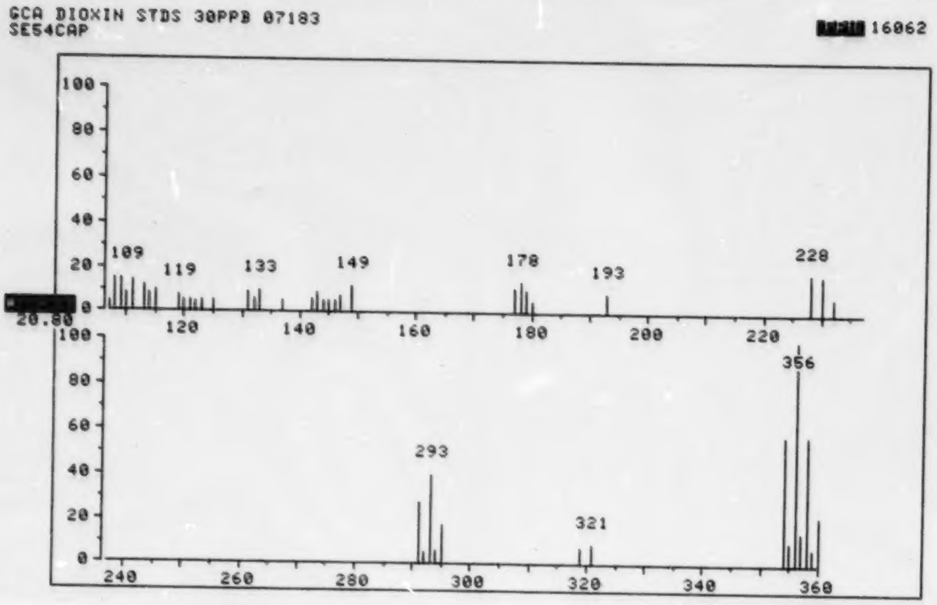


Figure 13. Molecular ion isotope cluster for pentachlorodibenzo-p-dioxin in standard mixture (Retention time 20.8 min).

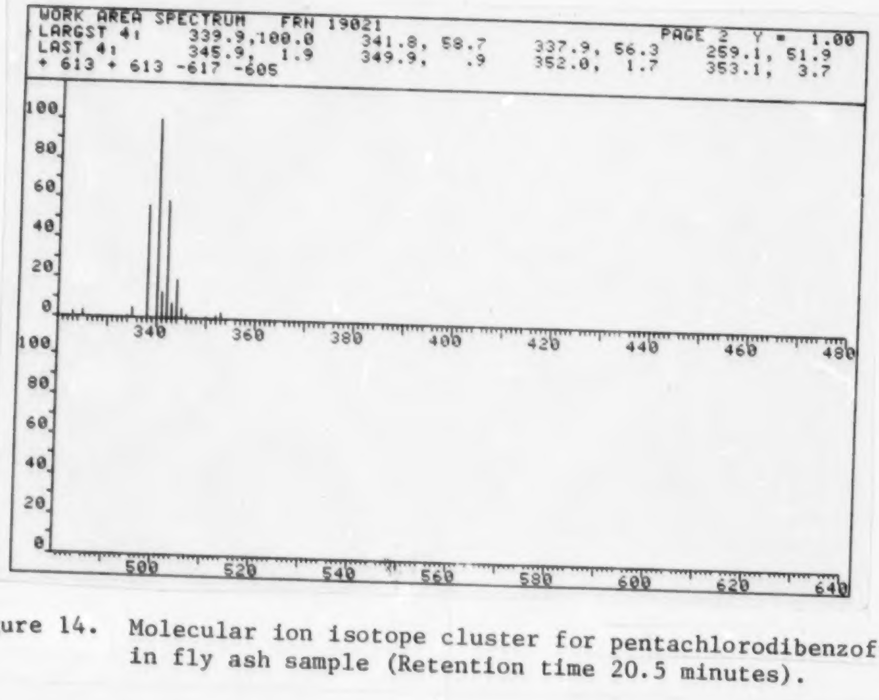


Figure 14. Molecular ion isotope cluster for pentachlorodibenzofuran in fly ash sample (Retention time 20.5 minutes).

EP Toxicity--

The fly ash samples were subjected to Extraction Procedure (EP) leachate generation as outlined in Reference 13. Sample aliquots were extracted for a period of 24 hours in an aqueous medium with the pH maintained at or below 5 using 0.5N acetic acid. The generated leachate was subsequently analyzed for arsenic, cadmium, total chromium, and lead by means of Inductively Coupled Argon Plasma Emission Spectroscopy (ICAP) utilizing a Jarrell Ash Model 855 Atom Comp.

# REFERENCES

1. "Sampling and Analysis Methods for Hazardous Waste Incineration," prepared for U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina (Contract No. 68-02-3111).
2. Evaluation of Methods for Analysis of Hazardous Wastes: Manual for Collaborators, Battelle Columbus Laboratories, 1981.
3. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, July 1982.
4. Ettre, L. S., Selective Detection for Column Chromatography, J. Chromatogr. Sci., 16, 396-417, 1978.
5. Standard Test Method for Sulfur in Petroleum Products (General Bomb Method), ANSI/ASTM D 129-64.
6. Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method), ANSI/ASTM D 808-63.
7. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, Revised March 1983.
8. Hanson, R. L., C. R. Clark, R. L. Carpenter and C. H. Hobbs, Evaluation of Tenax-GC and XAD-2 as Polymer Adsorbents for Sampling Fossil Fuel Combustion Products Containing Nitrogen Oxides, Envir. Sci. Technol., 15, 701-705, 1981.
9. Hunt, G. T., N. Pangaro and S. G. Zelenski, The Chemical Characterization of Potential Organic Interferences in Two Commercially Available Polymeric Adsorbents, Analytical Letters, 13, 521-528, 1980.
10. Hunt, G. T. and N. Pangaro, Potential Contamination from the Use of Synthetic Adsorbents in Air Sampling Procedures, Anal. Chem., 54(3), 369-372, 1982.
11. Lockmiller, C. H., M. W. Ewalt and E. C. Jensen, The Utility of Porous Polymer Sorbents in Chemically-Active Environments, Internal J. Environ. Anal. Chem., 8, 37-48, 1980.

12. Mass Spectrometry Review, 1981, 1, 29-62, John Wiley & Sons.

13. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Second Edition, SW-846, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., July 1982.

## SECTION 6

## QUALITY ASSURANCE

### INTRODUCTION

This section briefly summarizes QA/QC activity on this project since the issuance of the Work Plan in May 1982. Subsections deal with Sampling and Field Measurements QC, Laboratory Analysis QC, Performance and System Audits and Quality Control Problems and Corrective Actions. To curtail the size of this section, most raw QC data (instrument calibration data sheets, custody forms, analysts notebook pages, etc.) have been omitted. However, the Analytical QC subsection contains data reports for most, but not all of the QC samples specific to this project.

A combined Test/QA Plan was prepared in June 1982 and revised twice; the current revision is dated June 1983. A system audit was conducted in July 1983 to check on adherence to this QA Plan; the summary audit report is included in this section.

### SAMPLING AND FIELD MEASUREMENTS QUALITY CONTROL

Quality control procedures implemented during the field sampling deal mainly with equipment calibration, sampling procedures, field data reduction, and sample chain-of-custody. Specific activities are summarized below.

#### Equipment Calibration

Equipment and instrumentation used during the project participated in GCA's routine preventive maintenance and calibration program. Calibration of the equipment used for reference method testing was performed in accordance with the procedures outlined in the EPA publication "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III: Stationary Source Specific Methods". Calibration work sheets for the dry gas meters, orifices, pitot tubes, thermocouples and sample nozzles are presented in Appendix C of this report. Calibration of the carbon monoxide and oxygen continuous monitors was performed at the beginning and end of each one hour test run. All calibrations were within tolerance.

Gravimetric determinations were performed in GCA's environmentally controlled balance room. Room conditions are maintained at less than 50 percent relative humidity and at 15° to 25°C; actual conditions are recorded daily by the balance room technician. The Mettler H54 balance was used to weigh particulate filters and the Mettler H-15 balance was used to weigh the front-half rinses that were dried down in beakers. Each balance was checked with Class S weights in the approximate weight range of the sample before and after each weighing session. Blanks were weighed with each set of samples and were included in all final calculations for weight determinations.

### Sampling Procedures and Field Data Reduction

The personnel involved in the field activities of this project implemented sampling procedures in accordance with GCA's Test/QA Plan and EPA protocols. Leak checks of the sampling system and its components were performed prior to and at the end of each run. This information and all other pertinent sampling data were recorded on designated sampling forms. At the end of the initial background burn at GCA, the data forms were carefully reviewed by the field operations QC Coordinator for clarity and completeness. A memo citing deficiencies was issued and data sheets from all subsequent runs were spot-checked by the QC Coordinator.

The percent isokinetic flow was calculated manually in the field using standarized calculation forms to ensure valid sampling conditions. The majority of the source sampling data was reduced using a Texas Instruments TI-59 Desk Top Calculator with printer at GCA. These data were checked by two members of the field crew before being submitted to the field team leader for use in the individual summary reports.

### Chain-of-Custody Procedures

Chain-of-custody of all samples collected was initiated in the field. All samples were clearly labeled, sealed and their level marked prior to storage for shipment to GCA. Each sample was listed on the packing sheet/custody form to document its collection and the responsible field sample custodian. Sample codes, as designated on the Field/Laboratory Coordination Form and in the Test/QA Plan were followed throughout the program;. At GCA, custody of the samples was transferred to the Sample Bank Manager who logged the samples in the Master Log and assigned a GCA Control Number to each sample. This control number identified each sample throughout all further handling and analysis.

## LABORATORY ANALYSIS QUALITY CONTROL

Quality Control (QC) protocols implemented for this program, as specified in the Program Test and Quality Assurance Plan, included the use of method blanks, field-biased blanks, laboratory control spikes, blind spikes and a series of deuterated spikes contained in each sample designated for GC/MS analysis. A brief synopsis of each of these control elements is provided below. A more detailed discussion of each element, including results for each analytical category, is provided in subsequent portions of this section.

## Blank Samples

### Method Blanks--

Appropriate method blanks containing all reagents used in the preparation and analysis of samples were processed through the entire analytical scheme to assess spurious contamination arising from reagents, glassware and other materials used in the analysis. All reported data have been corrected by an appropriate method blank.

### Field-Biased Blanks--

Blank filters and reagents used in the collection of samples accompanied actual samples during transfer in the field and transfer to the sample bank for storage to account for contamination which might be introduced during these operations.

### Calibration Blanks--

These are blanks which are used in instrument calibration and contain all reagents used in the preparation of calibration standards except the standard itself.

## Laboratory Control Samples

Laboratory Control Samples (LCS) include both replicate samples and spiked samples (i.e., those fortified with predetermined quantities of the components of interest) which accompany program samples throughout the analytical scheme. Results from the analysis of control samples can provide information on analytical precision and spike recovery.

## Instrument Check Samples

These samples are usually prepared from an EPA/EMSL concentrate or other suitable reference material and are used on a daily basis to verify existing instrument calibration. Results from the analysis of these check samples are entered in the instrument logbook.

## Surrogate Spikes

Samples requiring analysis by GC/MS are routinely surrogate-spiked with a series of deuterated analogues of the components of interest. During this program, each sample requiring analysis for semivolatile organics was spiked with a mixture containing $d_5$-phenol, $d_3$-trichlorobenzene, $d_{10}$-biphenyl, and $d_{12}$-chrysene. It was anticipated that these compounds would assess the behavior of actual components in individual program samples during the entire preparative and analysis scheme.

## "Blind" Quality Control Samples

These may include both spiked samples and replicate samples which are prepared by the laboratory quality control coordinator. These samples are coded with GCA control numbers reserved for this purpose and inserted through the sample bank manager in order to mimic actual program samples. The origin and contents of these samples are unknown to the analyst. During this program, particulate and filter samples requiring organic and inorganic analysis and impingers requiring analysis for chloride were inserted as blind QC samples.

A summary of results for each of these quality control elements is provided in subsequent portions of this section.

## Fuel Feed

### Volatile Organics--

Volatile organic compounds in the fuel feed were determined using the tetraglyme procedure described in Section 5 of this report. Samples of a well-characterized oil were spiked to contain known quantities of a number of volatile compounds and analyzed with project samples using the tetraglyme procedure. A summary of these results is presented in Table 28. Replicate analyses were performed on a number of samples during the program. Table 29 presents typical data for the analysis of volatile organics in triplicate aliquots of a waste oil.

### Semivolatile Organics--

Analysis for semivolatile organic components in the fuel feed were performed using the GC/ECD techniques described in Section 5 of this report. Initially, analysis of the fuel feed samples was performed using silica gel chromatographic cleanup and GC/MS techniques. However, quality control results indicated that the accuracy of the trichlorobenzene and trichlorophenol data obtained using that technique was questionable, therefore, the GC/ECD procedure was substituted. Quality Control data for the analysis of semivolatiles in waste oil by GC/ECD are presented in Tables 30 through 32.

### Trace Metals--

The metal content of the fuel feed was determined using the procedures described in Section 5 of this report. In order to monitor the precision and accuracy of these analyses, aliquots of two appropriate NBS Standard Reference Materials (SRMs) were analyzed with project samples. NBS SRM 1634a, Trace Elements in Fuel Oil, was initially used as a laboratory control sample. However, a number of the elements contained in this sample were at or near detection limit in solution making accurate quantitation difficult. NBS SRM 1085, Wear Metals in Lubricating Oil, became available during this program and was also used as a laboratory control sample. SRM 1085 contains significantly higher levels of a number of elements of interest precluding some of the difficulties noted in the use of SRM 1634a. Data from analysis of the SRMs are presented in Tables 33 and 34.

Replicate aliquots of a number of submitted samples were carried through the preparation and analysis procedures to assess analytical precision; typical data for these replicate analyses are shown in Tables 35 and 36.

### Sulfur and Chloride--

The determination of sulfur and total chlorine in oil samples was performed using the Parr Bomb combustion technique with subsequent quantitation as described in Section 5. NBS SRM 1619; Sulfur in Residual Fuel

### TABLE 28. QUALITY CONTROL RESULTS - ANALYSIS OF OIL SAMPLES FOR VOLATILE ORGANICS - CONCENTRATION (mg/kg)

| Sample Identification | Site | Chloroform |  |  | 1,1,1-Trichloroethane |  |  | Trichloroethene |  |  | Tetrachloroethene |  |  | Toluene |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Reported | Expected | Recovery (%) | Reported | Expected | Recovery (%) | Reported | Expected | Recovery (%) | Reported | Expected | Recovery (%) | Reported | Expected | Recovery (%) |
| QC 298 | E/F | 3,500 | 4,200 | 83 | ND[a] | b | -- | 3,300 | 3,200 | 100 | 4,900 | 4,200 | 120 | 3,900 | 4,500 | 87 |
| QC 299 | E/F | 2,800 | 3,100 | 90 | ND[a] | b | -- | 2,300 | 2,400 | 96 | 3,200 | 3,100 | 100 | 2,800 | 3,400 | 82 |
| QC 300 | E/F | 3,600 | 3,600 | 100 | ND[a] | b | -- | 3,100 | 2,800 | 110 | 4,200 | 3,600 | 120 | 3,700 | 3,900 | 95 |
| QC 357[c] | A/C | ND[a] | b | -- | 170 | b | -- | ND[a] | b | -- | 120 | b | -- | 800 | b | -- |
| QC 358 | A/C | 2,900 | 3,300 | 88 | 2,800 | 3,900 | 72 | 3,200 | 4,100 | 78 | 4,800 | 4,100 | 130 | 4,200 | 3,500 | 120 |
| QC 359 | A/C | 3,500 | 3,600 | 97 | 3,500 | 4,300 | 81 | 5,000 | 3,700 | 140 | 5,900 | 4,600 | 130 | 5,000 | 3,900 | 130 |
| QC 360 | A/C | 3,400 | 3,700 | 92 | 3,600 | 4,400 | 82 | 3,700 | 3,800 | 97 | 6,000 | 4,700 | 130 | 4,900 | 4,000 | 120 |
| QC 493[c] | D/G | ND[a] | b | -- | Trace[d] | b | -- | ND[a] | b | -- | ND[a] | b | -- | ND[a] | b | -- |
| QC 494 | D/G | 4,500 | 3,800 | 120 | 3,500 | 2,900 | 120 | 3,500 | 4,000 | 86 | 4,000 | 4,000 | 100 | ND[a] | b | -- |
| QC 495 | D/G | 5,500 | 4,400 | 130 | 4,500 | 3,400 | 130 | 4,200 | 4,700 | 89 | 5,000 | 4,700 | 110 | ND[a] | b | -- |
| QC 496 | D/G | 5,700 | 4,500 | 130 | 4,800 | 3,500 | 140 | 4,600 | 4,900 | 94 | 4,800 | 4,900 | 98 | ND[a] | b | -- |
| QC 499[c] | D/G | Trace[d] | b | -- | Trace[d] | b | -- | ND[a] | b | -- | Trace[d] | b | -- | ND[a] | b | -- |
| QC 501 | D/G | 5,000 | 4,500 | 110 | 3,700 | 3,500 | 110 | 4,000 | 4,800 | 83 | 4,400 | 4,800 | 92 | ND[a] | b | -- |
| QC 502 | D/G | 4,600 | 3,900 | 120 | 3,500 | 3,000 | 120 | 4,000 | 4,200 | 95 | 5,000 | 4,200 | 120 | ND[a] | b | -- |
| Average Percent Recovery ($\bar{x}$) |  |  |  | 110 |  |  | 110 |  |  | 97 |  |  | 110 |  |  | 110 |
| Standard Deviation ($S_x$) |  |  |  | 17 |  |  | 25 |  |  | 17 |  |  | 13 |  |  | 20 |
| Relative Standard Deviation (%) |  |  |  | 15 |  |  | 23 |  |  | 18 |  |  | 12 |  |  | 18 |

[a] ND = <30 mg/kg

[b] Component not spiked.

[c] Background oil only. Background analysis results were used to correct spikes for any components native to the matrix.

[d] Trace = <100 mg/kg

TABLE 29. QUALITY CONTROL DATA--ANALYSIS OF VOLATILE ORGANICS IN TRIPLICATE ALIQUOTS OF GCA NO. 29466 (SITE A, RUN 9, WASTE FEED COMPOSITE)

| Parameter | Reported (μg/g) | | | $\overline{X}$ | $S_x$ | Relative standard deviation (%) |
|---|---|---|---|---|---|---|
| | 29466A | 29466B | 29466C | | | |
| Chloroform | 2,700 | 2,700 | 3,600 | 3,000 | 520 | 17 |
| Trichloroethane | 2,500 | 2,600 | 3,100 | 2,700 | 320 | 12 |
| Trichloroethylene | 2,700 | 3,000 | 3,600 | 3,100 | 460 | 15 |
| Tetrachloroethylene | 5,800 | 5,100 | 6,600 | 5,800 | 750 | 13 |

### TABLE 30. QUALITY CONTROL RESULTS--GC/ECD ANALYSIS OF SEMIVOLATILES IN WASTE OIL

| QC No. | 1,2,4-Trichlorobenzene Expected (mg/kg) | 1,2,4-Trichlorobenzene Recovered (mg/kg) | 1,2,4-Trichlorobenzene % Recovered | 1-chloronaphthalene Expected (mg/kg) | 1-chloronaphthalene Recovered (mg/kg) | 1-chloronaphthalene % Recovered |
|---|---|---|---|---|---|---|
| 543 | 2,400 | 2,300 | 96 | 2,600 | 2,800 | 108 |
| 544 | 2,500 | 2,200 | 88 | 2,800 | 3,600 | 128 |
| 545 | 2,400 | 2,200 | 92 | 2,600 | 2,600 | 100 |
| 546 | 2,400 | 2,100 | 87 | 2,600 | 2,700 | 104 |
| 547 | 2,600 | 2,400 | 92 | 2,800 | 3,000 | 107 |
| Average Percent Recovery | | | 91 | | | 109 |

TABLE 31. QUALITY CONTROL RESULTS--GC/ECD ANALYSIS OF TRICHLOROPHENOL IN WASTE OIL

| QC No. | Concentration (mg/kg) |  | Percent Recovery |
|---|---|---|---|
|  | Added | Recovered |  |
| 549 A | 2,000 | 2,000 | 100 |
| 549 B | 2,100 | 2,200 | 105 |
| 549 C | 2,000 | 2,200 | 110 |
| Average Percent Recovery |  |  | 105 |

TABLE 32. QUALITY CONTROL RESULTS--GC/ECD ANALYSIS OF SEMIVOLATILES IN DUPLICATE WASTE OIL ALIQUOTS

| GCA Control No. | Site | Run | Concentration (mg/kg) | | |
|---|---|---|---|---|---|
| | | | 1,2,4-Trichlorobenzene | 2-Chloronaphthalene | 2,4,5-Trichlorophenol |
| 28801A | F | 3 | 3,000 | 2,900 | 650 |
| 28801B | F | 3 | 3,200 | 2,800 | 690 |
| 29470A | A | 7 | 1,800 | 1,300 | 1,100 |
| 29470B | A | 7 | 1,700 | 1,200 | 1,100 |
| 29507A | C | 3 | 2,400 | 2,100 | 2,400 |
| 29507B | C | 3 | 2,300 | 2,000 | 2,400 |
| 30528A | G | 2 | 1,600 | 1,400 | a |
| 30528B | G | 2 | 1,700 | 1,500 | a |
| 31062A | D | 2 | 1,800 | 1,500 | a |
| 31062B | D | 2 | 1,800 | 1,400 | a |

[a] Component not spiked.

TABLE 33. ANALYSIS OF NBS STANDARD REFERENCE MATERIAL 1634a (TRACE ELEMENTS IN FUEL OIL)

| Element | NBS value (µg/g) | Reported (µg/g) | | | | | | Relative standard deviation (%) | Average recovery (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | 11/30/82 | 12/21/82 | 2/11/83 | 2/11/83 | $\bar{x}$ | $S_x$ | | |
| Calcium | 16[a] | 15.3 | 18.3 | 18.4 | 17.9 | 17.5 | 1.47 | 8.4 | 114 |
| Cobalt | 0.3[a] | 0.222 | 0.392 | 0.245 | 0.341 | 0.300 | 0.080 | 27 | 100 |
| Chromium | 0.7[a] | 0.644 | 0.727 | 0.667 | 0.660 | 0.675 | 0.036 | 5.3 | 96 |
| Iron | 31[a] | 25.3 | 27.7 | 34.1 | 26.9 | 28.5 | 3.86 | 14 | 92 |
| Nickel | 29±1[b] | 23.8 | 50.6[c] | 25.3 | 23.8 | 24.3 | 0.866 | 3.6 | 84 |
| Sodium | 87±4[b] | 73.9 | 81.8 | 67.6 | 73.9 | 74.3 | 5.78 | 7.8 | 85 |
| Vanadium | 56±2[b] | 46.9 | 53.3 | 53.0 | 46.9 | 50.0 | 3.61 | 7.2 | 89 |
| Zinc | 2.7±0.2[b] | 2.97 | 3.07 | 2.01 | 2.52 | 2.64 | 0.485 | 18 | 98 |

[a] NBS supplemental information.

[b] NBS Certified value.

[c] Rejected as outlier using Dixon Criteria for Testing of Extreme Observation (Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 1, EPA-600/9-76-005, U.S. EPA, Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C.).

TABLE 34. QUALITY CONTROL RESULTS--ANALYSIS OF NBS SRM 1085 (WEAR METALS IN LUBRICATING OIL)

| Element | NBS value (µg/g) | Reported (µg/g) | | | | | $\bar{x}$ | $S_x$ | Relative standard deviation (%) | Average recovery (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 4/26/83 | | 7/1/83 | | | | | | |
| | | A | B | A | B | C | | | | |
| Aluminum | 296±4 | 284 | 278 | 231[a] | 276 | 277 | 279 | 3.59 | 1.3 | 94 |
| Chromium | 298±5 | 292 | 278 | 205[a] | 274 | 258 | 276 | 14.0 | 5.1 | 93 |
| Copper | 295±10 | 262 | 253 | 213[a] | 270 | 265 | 263 | 7.14 | 2.7 | 89 |
| Iron | 300±4 | 268 | 252 | 212[a] | 256 | 274 | 263 | 10.2 | 3.4 | 88 |
| Lead | 305±8 | 298 | 300 | 255[a] | 302 | 297 | 299 | 2.22 | 0.74 | 98 |
| Magnesium | 297±3 | 327 | 327 | 201[a] | 277 | 277 | 302 | 28.9 | 9.6 | 102 |
| Molybdenum | 292±11 | 286 | 282 | 233[a] | 287 | 287 | 286 | 2.38 | 0.83 | 98 |
| Nickel | 303±7 | 283 | 269 | 259 | 297 | 295 | 281 | 16.5 | 5.6 | 93 |

[a] Rejected as outlier using Dixon Criteria for Testing of Extreme Observation (Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 1, EPA-600/9-76-005, U.S. EPA, Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C.).

TABLE 35. QUALITY CONTROL DATA--ANALYSIS OF METALS IN TRIPLICATE ALIQUOTS OF GCA NO. 28799 (WASTE OIL SITE F, RUN 1)

|  | Reported (μg/g) |  |  |  |  |  |
|---|---|---|---|---|---|---|
| Element | 28799A | 28799B | 28799C | $\overline{X}$ | $S_x$ | Relative standard deviation (%) |
| Aluminum | 18.4 | 14.7 | 24.6 | 19.2 | 5.0 | 26 |
| Antimony | <0.4 | <0.4 | 0.8 | --- | --- | --- |
| Arsenic | 9.9 | 8.4 | 8.7 | 9.0 | 0.79 | 8.8 |
| Barium | 56.1 | 55.0 | 55.0 | 55.4 | 0.64 | 1.2 |
| Beryllium | 0.04 | 0.03 | 0.05 | 0.04 | 0.01 | 25 |
| Boron | 3.93 | 6.60 | 7.23 | 5.92 | 1.75 | 30 |
| Cadmium | 1.96 | 2.12 | 2.19 | 2.09 | 0.12 | 5.7 |
| Calcium | 751 | 753 | 763 | 756 | 6.4 | 0.85 |
| Chromium | 7.89 | 7.37 | 8.32 | 7.86 | 0.48 | 6.1 |
| Cobalt | 0.26 | 0.22 | 0.32 | 0.27 | 0.05 | 19 |
| Copper | 47.7 | 51.3 | 50.9 | 50.0 | 1.97 | 3.9 |
| Iron | 177 | 156 | 217 | 183 | 31.0 | 17 |
| Lead | 1,380 | 1,380 | 1,360 | 1,370 | 11.5 | 0.84 |
| Magnesium | 197 | 185 | 196 | 193 | 6.66 | 3.5 |
| Manganese | 6.68 | 6.86 | 7.39 | 6.98 | 0.37 | 5.3 |
| Molybdenum | 3.74 | 3.62 | 3.66 | 3.67 | 0.061 | 1.7 |
| Nickel | 2.7 | 2.3 | 3.4 | 2.80 | 0.56 | 20 |
| Selenium | < 0.4 | < 0.4 | < 0.4 | --- | --- | --- |
| Silicon | 26.6 | 20.8 | 27.4 | 24.9 | 3.6 | 14 |
| Silver | < 0.02 | < 0.02 | < 0.02 | --- | --- | --- |
| Sodium | 117 | 123 | 131 | 124 | 7.02 | 5.7 |
| Strontium | 0.93 | 1.01 | 1.09 | 1.01 | 0.08 | 7.9 |
| Thallium | < 0.8 | < 0.8 | < 0.8 | --- | --- | --- |
| Tin | 3.0 | 4.1 | 4.7 | 3.93 | 0.86 | 22 |
| Titanium | 4.92 | 3.18 | 5.82 | 4.64 | 1.34 | 29 |
| Vanadium | 3.4 | 3.5 | 4.0 | 3.63 | 0.32 | 8.8 |
| Zinc | 630 | 685 | 690 | 668 | 33.3 | 5.0 |

TABLE 36. QUALITY CONTROL DATA--ANALYSIS OF METALS IN TRIPLICATE ALIQUOTS OF GCA NO. 28802 (WASTE OIL SITE F, RUN 4)

| Element | Reported (μg/g) | | | $\bar{X}$ | $S_x$ | Relative standard deviation (%) |
|---|---|---|---|---|---|---|
| | 28802A | 28802B | 28802C | | | |
| Aluminum | 38.9 | 37.8 | 40.8 | 39.2 | 1.52 | 3.9 |
| Antimony | < 0.4 | < 0.4 | 1.9 | --- | --- | --- |
| Arsenic | 8.9 | 7.5 | 7.9 | 8.1 | 0.72 | 8.9 |
| Barium | 57.6 | 56.8 | 57.5 | 57.3 | 0.44 | 0.77 |
| Beryllium | 0.05 | 0.05 | 0.06 | 0.05 | 0.006 | 12 |
| Boron | 4.44 | 5.89 | 5.26 | 5.20 | 0.73 | 14 |
| Cadmium | 2.90 | 2.91 | 2.70 | 2.77 | 0.12 | 4.3 |
| Calcium | 675 | 700 | 709 | 695 | 17.6 | 2.5 |
| Chromium | 12.5 | 11.7 | 12.7 | 12.3 | 0.53 | 4.3 |
| Cobalt | 0.42 | 0.41 | 0.44 | 0.42 | 0.015 | 3.6 |
| Copper | 56.2 | 59.7 | 59.8 | 58.6 | 2.05 | 3.5 |
| Iron | 250 | 247 | 258 | 252 | 5.69 | 2.3 |
| Lead | 1,230 | 1,210 | 1,230 | 1,220 | 11.5 | 0.94 |
| Magnesium | 179 | 177 | 179 | 178 | 1.15 | 0.65 |
| Manganese | 8.09 | 8.62 | 8.86 | 8.52 | 0.39 | 4.6 |
| Molybdenum | 3.51 | 3.65 | 3.77 | 3.64 | 0.13 | 3.6 |
| Nickel | 6.0 | 5.6 | 6.3 | 5.97 | 0.35 | 5.9 |
| Selenium | < 0.4 | < 0.4 | < 0.4 | --- | --- | --- |
| Silicon | 49.4 | 47.8 | 52.2 | 49.8 | 2.23 | 4.5 |
| Silver | 0.42 | 0.45 | 0.44 | 0.44 | 0.015 | 3.4 |
| Sodium | 125 | 138 | 139 | 134 | 7.81 | 5.8 |
| Strontium | 0.98 | 1.13 | 1.19 | 1.10 | 0.11 | 10 |
| Thallium | < 0.8 | < 0.8 | < 0.8 | --- | --- | --- |
| Tin | 5.6 | 5.8 | 6.6 | 6.0 | 0.53 | 8.8 |
| Titanium | 10.2 | 9.91 | 10.3 | 10.1 | 0.20 | 2.0 |
| Vanadium | 8.3 | 8.8 | 9.0 | 8.7 | 0.36 | 4.1 |
| Zinc | 564 | 616 | 622 | 600 | 31.9 | 5.3 |

Oil, was used to monitor the sulfur analysis; these results are summarized in Table 37.

In order to assess the analysis of total chlorine, aliquots of mineral oil were spiked with known quantities of chlorobenzene and analyzed with project samples. An unspiked aliquot of mineral oil was used for the blank correction of the laboratory control samples. These results are presented in Table 38.

Duplicate aliquots of a number of samples were prepared and analyzed for sulfur and chlorine. Typical data for these replicate analyses are presented in Table 39.

## Physical Properties

Analyses for physical properties were performed by Gilbert/Commonwealth, Reading, PA. All instruments used in these analyses were calibrated daily with calibration verified through analysis of a known QC sample. Duplicate analyses were performed on every tenth sample.

## Flue Gas

### Volatile Organics--

Quality control protocols for the analysis of volatile organics in flue gas samples included analysis of replicates and laboratory control samples. In addition, the accuracy of the calibration standards was periodically checked against gas generated from VICI/Metronics Dynacal permeation tubes which have been certified against NBS traceable standards.

Data from the analysis of permeation tube standards against GC/ECD standards are presented in Table 40. These samples were also analyzed by GC/MS against independently prepared GC/MS standards; a comparison of the GC/MS and GC/ECD results are presented in Table 41. The loss of tetrachloroethylene noted in the GC/MS analysis of sample numbers 603 and 604 was determined to be due to improper storage of the sample prior to analysis. Replicate results for all samples analyzed by GC/ECD were within 10 percent.

Quality control procedures for Tenax analysis included analysis of spiked tubes and analysis of tubes spiked by personnel at EPA/RTP. Table 42 presents typical data from the analysis of spiked tubes. The poor precision makes accurate quantitation difficult; the cause for this problem could not be isolated during the program. The difficulties associated with the the Tenax analysis are further illustrated by the results of the performance samples, presented in Table 43. It appears that the Tenax results obtained in this program can be used to confirm qualitative results obtained by GC/ECD but cannot be considered quantitative.

### Semivolatile Organics--

Quality control procotols for the analysis of semivolatile organics in Method 5 train samples included the use of surrogates and analysis of laboratory control samples and blind quality control samples. Each of the

TABLE 37. ANALYSIS OF NBS STANDARD REFERENCE MATERIAL 1619 (SULFUR IN RESIDUAL FUEL OIL)

| Sample | NBS value (sulfur weight %) | Date | Reported (sulfur weight %) |
|---|---|---|---|
| NBS SRM 1619 | 0.719 ± 0.007 | 10/18/82 | 0.72 |
| | | 10/18/82 | 0.86 |
| | | 11/01/82 | 0.88 |
| | | 11/16/82 | 0.68 |
| | | 02/08/83 | 0.66 |
| | | 02/10/83 | 0.64 |
| Average Percent Recovery ($\bar{x}$) | | | 0.74% sulfur |
| Standard Deviation ($S_x$) | | | 0.10 |
| Relative Standard Deviation | | | 14% |
| Average Recovery | | | 103% |

TABLE 38. ANALYSIS OF SPIKED MINERAL OIL FOR CHLORINE

| Sample identification | Total Chlorine (μg/g) |  | Percent recovery |
|---|---|---|---|
|  | Reported | Expected |  |
| QC-1 | 231 | 229 | 101 |
| QC-2 | 219 | 229 | 96 |
| QC-3 | 1,200 | 1,440 | 83 |
| QC-4 | 510 | 596 | 86 |
| QC-5 | 479 | 577 | 83 |

Average Percent Recovery ($\bar{x}$) = 90

Relative Standard Deviation (%) = 9.1

## TABLE 39. ANALYSIS OF CHLORINE AND SULFUR IN DUPLICATE WASTE OIL ALIQUOTS

| GCA Control No. | Site | Run | Parameter | Reported (%) A | Reported (%) B |
|---|---|---|---|---|---|
| 28512 | E | 1 | Chlorine | 0.695 | 0.712 |
| 29471 | A | 8 | Chlorine | 1.08 | 1.01 |
| 29505 | C | 1 | Chlorine | 0.843 | 0.715 |
| 28512 | E | 1 | Sulfur | 0.638 | 0.688 |
| 28513 | E | 2 | Sulfur | 0.631 | 0.658 |

TABLE 40. QUALITY CONTROL RESULTS--PERMEATION TUBE STANDARDS CHECK BY GC/ECD

| Sample identification | Parameter | Reported ($\mu g/m^3$) | Theoretical ($\mu g/m^3$) | Percent recovery |
|---|---|---|---|---|
| QC 603 | Tetrachloroethylene | 190 | 220 | 86 |
| QC 604 | Tetrachloroethylene | 450 | 450 | 100 |
| QC 608 | Chloroform | 300 | 300 | 100 |
| QC 609 | Chloroform | 440 | 450 | 98 |
| QC 610 | Trichloroethane | 360 | 370 | 97 |
| QC 611 | Trichloroethane | 460 | 450 | 102 |
| QC 612 | Trichloroethylene | 380 | 280 | 136 |
| QC 613 | Trichloroethylene | 480 | 420 | 114 |
|  |  |  | Average = | 104% |

TABLE 41. COMPARISON OF GC/MS AND GC/ECD RESULTS FOR PERMEATION TUBE STANDARDS

| Sample identification | Parameter | Reported µg/m$^3$ GC/ECD | Reported µg/m$^3$ GC/MS | Theoretical (µg/m$^3$) |
|---|---|---|---|---|
| QC 603 | Tetrachloroethylene | 190 | 8.8 | 220 |
| QC 604 | Tetrachloroethylene | 450 | ND | 450 |
| QC 608 | Chloroform | 300 | 360 | 300 |
| QC 609 | Chloroform | 440 | 640 | 450 |
| QC 610 | Trichloroethane | 360 | 460 | 370 |
| QC 611 | Trichloroethane | 460 | 820 | 450 |
| QC 612 | Trichloroethylene | 380 | 440 | 280 |
| QC 613 | Trichloroethylene | 480 | 560 | 420 |

## TABLE 42. QUALITY CONTROL RESULTS--TENAX ANALYSIS

| Parameter | Expected (ng) | Reported Values (ng) | | | | | $\overline{X}$ | $S_x$ | Relative Standard Deviation (%) | Average Recovery (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 01/26/83 | | 01/28/83 | | | | | | |
| | | A | B | A | B | C | | | | |
| Chloroform | 730 | 1,300 | 1,200 | 500 | 660 | 500 | 830 | 390 | 47 | 114 |
| Trichloroethylene | 730 | 1,000 | 1,100 | 480 | 700 | 1,000 | 860 | 260 | 30 | 118 |
| 1,1,1-Trichloroethane | 700 | 530 | 410 | 440 | 460 | 320 | 430 | 77 | 18 | 61 |
| Perchloroethylene | 800 | 1,400 | 1,200 | 430 | 860 | 1,000 | 980 | 370 | 38 | 123 |
| Toluene | 930[a] | 1,100 | 1,100 | 420[b] | 1,100 | 1,300 | 1,200 | 100 | 8.3 | 129 |
| 1,1,2-Trichloroethane | 700 | 640 | 780 | 410 | 650 | 840 | 660 | 170 | 26 | 94 |
| Benzene | 930[a] | 1,300 | 1,400 | 530 | 890 | 1,100 | 1,000 | 350 | 35 | 110 |

[a] These values represent an average of 900 and 950 ng.

[b] This value was rejected using Dixon Criteria for Testing of Extreme Observation.

## TABLE 43. ANALYSIS OF TENAX CARTRIDGES FORTIFIED AT EMSL/RTP

| Sample Identification GCA number | Nanograms/Tube |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | EMSL-1 30464 |  | EMSL-2 30465 |  | EMSL-3 30466 |  | EMSL-4 30467 |  | EMSL-5 30468 |  | Field Biased Blank 30463 |  |
|  | Reported | Expected | Reported | Expected | Reported | Expected | Reported | Expected | Reported | Expected | Reported | Expected |
| Chloroform | 690 | 361 | 630 | 577 | 1,600 | 865 | 300 | 865 | 660 | 865 | ND | ND |
| Benzene | 780 | 341 | 2,500 | 544 | 2,500 | 809 | 140 | 554 | 380 | 554 | ND | ND |
| Trichloroethylene | 1,300 | 568 | 2,600 | 852 | 720 | 355 | 190 | 355 | 640 | 355 | ND | ND |
| 1,1,1-Trichloroethane | 1,400 | 844 | 800 | 584 | 530 | 325 | 280 | 325 | 330 | 325 | ND | ND |
| 1,1,2-Trichloroethane | 480 | ND | 370 | ND | 370 | ND | 290 | ND | 290 | ND | 150 | ND |
| Toluene[a] | — | — | — | — | — | — | — | — | — | — | ND | ND |
| Tetrachloroethylene[b] | — | 866 | 1,500 | 394 | 1,800 | 630 | 1,500 | 630 | 2,100 | 630 | 1,100 | ND |

[a] Quantitative results not reported because each cartridge contained levels above the highest standard (3400 ng). All six tubes are estimated to contain 4,000-5,000 ng/tube.

[b] EMSL-1 was above the range of the calibration curve; it is estimated to contain 3700 ng of tetrachloroethylene. The highest standard used was 3,200 ng.

add XAD

combined filter and probe rinse samples was surrogate spiked with a mixture containing $d_5$-phenol, $d_3$-trichlorobenzene, $d_{10}$-biphenyl, $d_{12}$-chrysene prior to extraction. Surrogate recoveries for each of the samples are presented in Table 44. A series of quality control samples consisting of 80-150 µg of the components of interest spiked onto a blank XAD/filter sample were prepared and analyzed with project samples; these results are presented in Table 45. A portion of the extract was reduced to 100 µl and analyzed for polychlorinated dibenzodioxins and dibenzofurans. A series of spiked samples were prepared and analyzed with project samples; these results are presented in Table 46. In addition, two blank QC samples consisting of National Bureau of Standards Standard Reference Material 1649--Urban Dust, Organics were submitted; these results are presented in Table 47.

Trace Metals--

Quality Control procedures for the analysis of trace elements in Method 5 train particulates consisted of analysis of laboratory control samples consisting of NBS SRM 1648, Urban Particulate, and a spiked Method 5 filter and analysis of a blind QC sample consisting of NBS SRM 1633, Coal Fly Ash. These results are presented in Tables 48 through 50.

Chloride--

Quality Control procedures for the determination of chloride in impinger samples included the analysis of an EPA/EMSL Cincinnati quality control sample and analysis of blind QC samples prepared by spiking the 1 N NaOH impinger solution with a known quantity of the chloride stock standard. These results are presented in Tables 51 and 52.

### Fly Ash

Organics--

Quality control procedures for the determination of organics in fly ash involved analysis of replicate aliquots and the use of surrogate spikes to monitor sample preparation and analysis. These results are presented in Tables 53 and 54.

Inorganics--

Quality control procedures for the analysis of metals and chloride involved analysis of replicate aliquots of project samples. Results from the analysis of replicate aliquots of GCA No. 31310, Fly Ash - Site D for trace elements are presented in Table 55. Two aliquots of GCA No. 27326, Site D Boiler Fly Ash, were subjected to the water leaching procedure described in Section 5 with the aqueous leach subsequently analyzed using ion chromatography. The reported values for the replicate aliquots are shown below:

| Sample Identification | Chloride (%) |
|---|---|
| 2732626A - Site D, Boiler Fly Ash | 0.310 |
| 2732626B - Site D, Boiler Fly Ash | 0.304 |

## TABLE 44. QUALITY CONTROL RESULTS--METHOD 5 TRAIN SURROGATE RECOVERIES

| GCA Control No. | Site | Run No. | Surrogate Recovery (%)[a] | | | |
|---|---|---|---|---|---|---|
| | | | $d_5$-phenol | $d_3$-trichlorobenzene | $d_{10}$-biphenyl | $d_{12}$-chrysene |
| 28467 | E | 2 | 75 | 74 | 82 | 95 |
| 28473 | E | 3 | 90 | 85 | 89 | 100 |
| 28479 | E | 4 | 90 | 83 | 96 | 90 |
| 28485 | E | 5 | 100 | 95 | 96 | 95 |
| 28491 | E | 6 | 95 | 88 | 93 | 100 |
| 28497 | E | Field-Biased Blank | 90 | 89 | 94 | 95 |
| 29411 | A | 4 | 87 | 95 | 90 | 100 |
| 29417 | A | 5 | 90 | 90 | 81 | 93 |
| 29423 | A | 6 | 90 | 81 | 81 | 87 |
| 29429 | A | 7 | 83 | 81 | 76 | 80 |
| 29441 | A | 9 | 90 | 86 | 81 | 83 |
| 29452 | A | Blank | 80 | 86 | 76 | 97 |
| 29481 | C | 2 | 77 | 86 | 76 | 97 |
| 29487 | C | 3 | 83 | 81 | 81 | 87 |
| 29492 | C | 4 | 96 | 86 | 90 | 63 |
| 29497 | C | Field-Biased Blank | 77 | 86 | 76 | 80 |
| 30495 | G | 2 | 90 | 95 | 81 | 83 |
| 30501 | G | 3 | 103 | 95 | 90 | 97 |
| 30507 | G | 4 | 97 | 95 | 86 | 40 |
| 30513 | G | Blank | 107 | 100 | 95 | 107 |
| 30518 | G | Field-Biased Blank | 100 | 95 | 90 | 93 |
| 31072 | D | 2 | 97 | 100 | 95 | 87 |
| 31077 | D | 3 | 103 | 95 | 90 | 67 |
| 31082 | D | 4 | 113 | 95 | 95 | 73 |
| 31087 | D | 5 | 110 | 90 | 95 | 73 |
| 31092 | D | 6 | 120 | 90 | 100 | 70 |
| 31097 | D | Field-Biased Blank | 113 | 90 | 85 | 77 |

(continued)

## TABLE 44 (continued)

| Laboratory Control Samples | Surrogate Recovery (%)[a] | | | |
|---|---|---|---|---|
| | $d_5$-phenol | $d_3$-trichlorobenzene | $d_{10}$-biphenyl | $d_{12}$-chrysene |
| QC 403 | 90 | 91 | 100 | 100 |
| QC 404 | 80 | 81 | 96 | 100 |
| QC 428 | 70 | 86 | 86 | 87 |
| QC 435 | 73 | 81 | 100 | 83 |
| QC 446 | 67 | 81 | 76 | 83 |
| QC 451 | 70 | 76 | 76 | 90 |
| QC 452 | 77 | 90 | 81 | 110 |
| QC 453 | 80 | 86 | 86 | 90 |
| QC 487 | 97 | 90 | 86 | 83 |
| QC 488 | 103 | 90 | 90 | 80 |
| QC 513 | 90 | 90 | 90 | 67 |
| QC 514 | 93 | 86 | 95 | 73 |
| Average Percent Recovery ($\bar{x}$) | 91 | 88 | 88 | 86 |
| Standard Deviation ($S_x$) | 13 | 6.0 | 7.6 | 14 |
| Relative Standard Deviation, % | 14 | 6.8 | 8.6 | 16 |

---

[a] 100 to 300 μg of each component was spiked onto the filter.

18

## TABLE 45. QUALITY CONTROL RESULTS--METHOD 5 TRAIN SPIKES

| Sample Identification | Component Recovery (%) | | |
|---|---|---|---|
| | 1,2,4-Trichlorobenzene | 2-Chloronaphthalene | 2,4,5-Trichlorophenol |
| QC 404 | 100 | 100 | 80 |
| QC 435 | 100 | 92 | 80 |
| QC 452 | 96 | 79 | 77 |
| QC 453 | 97 | 83 | 85 |
| QC 488 | 100 | 78 | 87 |
| QC 514 | 100 | 83 | 80 |
| Average Percent Recovery ($\bar{x}$) | 99 | 86 | 82 |
| Standard Deviation ($S_x$) | 1.8 | 8.5 | 3.7 |
| Relative Standard Deviation (%) | 1.8 | 9.9 | 4.5 |

TABLE 46. QUALITY CONTROL RESULTS--GC/MS ANALYSIS OF METHOD 5 TRAIN EXTRACTS FOR DIBENZOFURANS AND DIBENZODIOXINS

| Component | Total μg 557 | 558 | 559 | 574 | Expected | Average Recovery % |
|---|---|---|---|---|---|---|
| Dibenzofuran | 2.0 | 1.8 | 2.1 | 1.7 | 3.4 | 56 |
| Chlorodibenzodioxin | 1.6 | 1.6 | 1.6 | 1.4 | 4.8 | 32 |
| Dichlorodibenzodioxin | 4.2 | 3.8 | 3.7 | 3.4 | 5.1 | 74 |
| Dichlorobenzofuran | 3.7 | 3.3 | 3.4 | 3.3 | 5.0 | 68 |
| Octachlorodibenzodioxin | 2.5 | 2.2 | 2.9 | 1.8 | 5.8 | 41 |
| Octachlorodibenzofuran | 2.1 | 1.3 | 1.6 | 1.2 | 5.0 | 31 |

Samples were prepared for analysis by GC/MS following the alumina column chromatography procedures used for program samples which required cleanup prior to analysis. GC/MS analyses were performed in the Selected Ion Monitoring (SIM) mode.

TABLE 47. QUALITY CONTROL RESULTS--ANALYSIS OF NBS SRM 1649, URBAN DUST-ORGANICS (BLIND QC SAMPLES)

| Parameter | Concentration (μg/g) | | |
|---|---|---|---|
| | GCA No. 28781 | GCA No. 29492 | NBS Value |
| Phenanthrene/Anthracene | 3.8 | 8.3 | 4.5[b] |
| Fluoranthene | 8.0 | 8.8 | 7.1 ± 0.5[c] |
| Pyrene | 5.8 | 73 | 6.6[b] |
| Benzo(a)anthracene/chrysene | 13 | NR[a] | 6.2[b] |
| Benzo(k)fluoranthene/benzo(b)fluoranthene | 18 | NR[a] | 8.3[b] |

[a] NR = Not reported.

[b] NBS non-certified.

[c] NBS certified value.

TABLE 48. QUALITY CONTROL RESULTS--ANALYSIS OF NBS SRM 1648, URBAN PARTICULATE

| Element | NBS value | Concentration (μg/g)[a] Reported 4/19/83 | 5/13/83 | 5/27/83 | $\bar{x}$ | Relative standard deviation (%) | Average recovery (%) |
|---|---|---|---|---|---|---|---|
| Aluminum (%) | 3.42±0.11[b] | 3.0 | 3.2 | 3.1 | 3.1 | 3.2 | 91 |
| Antimony | 45[c] | 32 | 42 | 31 | 35 | 17 | 78 |
| Arsenic | 115±10[b] | 120 | 129 | 132 | 127 | 4.9 | 110 |
| Barium | 737[c] | 637 | 683 | 707 | 676 | 5.3 | 92 |
| Cadmium | 75±7[b] | 59 | 73.1 | 70.5 | 67.5 | 11 | 90 |
| Chromium | 403±12[b] | 116 | 128 | 119 | 121 | 5.2 | 30 |
| Cobalt | 18[c] | 17 | 21 | 21 | 20 | 12 | 110 |
| Copper | 609±27[b] | 513 | 566 | 554 | 544 | 5.1 | 89 |
| Iron (%) | 3.91±0.10[b] | 3.17 | 3.30 | 3.10 | 3.19 | 3.1 | 82 |
| Lead (%) | 0.655±0.008[b] | 0.481 | 0.649 | 0.545 | 0.558 | 15 | 85 |
| Magnesium (%) | 0.8[c] | 0.7 | 0.1[d] | 0.7 | 0.7 | --- | 88 |
| Manganese | 860[c] | 532 | 590 | 584 | 569 | 5.6 | 66 |
| Nickel | 82±3[b] | 100 | 83 | 76 | 86 | 14 | 105 |
| Sodium (%) | 0.40[c] | 0.27 | 0.43 | 0.46 | 0.39 | 26 | 98 |
| Vanadium | 130[c] | 97 | 107 | 102 | 102 | 4.9 | 78 |
| Zinc (%) | 4760±140[b] | 3360 | 5810 | 4040 | 4400 | 29 | 92 |

---

[a] Except as noted.

[b] NBS certified value.

[c] NBS non-certified value.

[d] Rejected as outlier using Dixon Criteria.

TABLE 49. QUALITY CONTROL RESULTS--LABORATORY CONTROL SAMPLE FOR ANALYSIS OF METALS ON METHOD 5 FILTERS

| Element | Reported (µg) | Expected (µg) | Percent recovery |
|---|---|---|---|
| Cadmium | 139 | 150 | 93 |
| Copper | 218 | 250 | 87 |
| Iron | 286 | 200 | 143 |
| Lead | 85.9 | 100 | 86 |
| Manganese | 68.4 | 75 | 91 |
| Vanadium | 102 | 100 | 102 |
| Zinc | 102 | 95 | 107 |

23

TABLE 50. QUALITY CONTROL RESULTS--ANALYSIS OF NBS SRM 1633, COAL FLY ASH, FOR TRACE METALS (BLIND QUALITY CONTROL SAMPLE - GCA NO. 29446)

| Element | Reported (μg/g) | NBS Value (μg/g) | Percent recovery |
|---|---|---|---|
| Arsenic | 32.2 | 61±6 | 53 |
| Beryllium | 13.8 | 12 | 115 |
| Cadmium | 1.68 | 1.45±0.06 | 116 |
| Chromium | 85.0 | 121±2 | 70 |
| Cobalt | 36.1 | 38 | 95 |
| Copper | 86.8 | 128±5 | 68 |
| Manganese | 286 | 493±7 | 58 |
| Nickel | 64.7 | 98±3 | 66 |
| Strontium | 1100 | 1380 | 80 |
| Vanadium | 169 | 214±8 | 79 |
| Zinc | 136 | 210±20 | 65 |

TABLE 51. QUALITY CONTROL RESULTS--ANALYSIS OF EPA MINERALS QC SAMPLE FOR CHLORIDE

| Sample | EPA Value (mg/l $Cl^-$) | Date | Reported (mg/l $Cl^-$) |
|---|---|---|---|
| EPA WP 478-3 (Minerals) | 21.5 | 2/03/83 | 20.5 |
| | | 2/04/83 | 20.4 |
| | | 2/07/83 | 19.7 |
| | | 3/08/83 | 20.5 |
| | | 3/09/83 | 21.0 |
| | | 3/10/83 | 20.5 |
| | | 3/21/83 | 22.3 |
| | | 3/22/83 | 20.8 |
| | | 4/06/83 | 22.9 |
| | | 4/07/83 | 20.8 |
| Average ($\bar{x}$) | | 20.9 mg/l $Cl^-$ | |
| Standard Deviation ($S_x$) | | 0.95 | |
| Relative Standard Deviation (%) | | 4.6 | |
| Average Recovery (%) | | 97 | |

### TABLE 52. QUALITY CONTROL RESULTS--CHLORIDE IN IMPINGER SOLUTIONS: ANALYSIS OF BLIND QC SAMPLES

| GCA No. | Sample identification | Reported (ng/l) | Expected (ng/l) | Percent recovery |
|---|---|---|---|---|
| 28783 | Blind QC Sample | 15.6 | 15 | 104 |
| 29448 | Blind QC Sample | 14.4 | 15 | 96 |

TYPING GUIDE SHEET

## TABLE 53. QUALITY CONTROL RESULTS--REPLICATE ANALYSIS OF GCA NO. 31310, FLY ASH, SITE D

| Parameter | Reported (mg/kg) | |
|---|---|---|
| | 31310-A | 31310-B |
| Dibenzofuran | 170 | 210 |
| Chlorodibenzofurans | 24 | ND |
| Dichlorodibenzofurans | ND | ND |
| Trichlorodibenzofurans | ND | ND |
| Tetrachlorodibenzofurans | 170 | 81 |
| Pentachlorodibenzofurans | 660 | 570 |
| Hexachlorodibenzofurans | 310 | 250 |
| Heptachlorodibenzofurans | 340 | 240 |
| Octachlorodibenzofurans | 26 | 19 |
| Dibenzodioxin | ND | ND |
| Chlorodibenzodioxins | ND | ND |
| Dichlorodibenzodioxins | ND | ND |
| Trichlorodibenzodioxins | ND | ND |
| Tetrachlorodibenzodioxins | ND | ND |
| Pentachlorodibenzodioxins | 58 | ND |
| Hexachlorodibenzodioxins | 90 | 58 |
| Heptachlorodibenzodioxins | 130 | 90 |
| Octachlorodibenzodioxins | 150 | 110 |

EPA-287 (Cin.) (4-76)

TABLE 54. QUALITY CONTROL RESULTS--GC/MS ANALYSIS OF FLY ASH SAMPLES: SURROGATE RECOVERIES, SITE D

| GCA Control No. | Surrogate total μg<br>$d_3$-trichlorobenzene | <br>$d_{10}$-biphenyl | <br>$d_{12}$-chrysene |
|---|---|---|---|
| 31308 | 210 | 250 | 80 |
| 31309 | 180 | 220 | 67 |
| 31310-1 | 290 | 310 | 110 |
| 31310-2 | 210 | 210 | 51 |
| 31311 | 220 | 150 | 210 |
| Expected (μg) | 210 | 210 | 300 |
| Average Recovery (%) | 100 | 110 | 35 |

Significant interferences from coeluting material prevented quantitation of the $d_5$-phenol surrogate added to the samples.

TABLE 55. QUALITY CONTROL RESULTS--REPLICATE ANALYSIS OF GCA NO. 31310, FLY ASH, SITE D FOR TRACE ELEMENTS

| Element | Reported (μg/g)[a] | |
|---|---|---|
| | 31310-A | 31310-B |
| Aluminum | 1730 | 1780 |
| Antimony | 34 | 36 |
| Arsenic | 166 | 175 |
| Barium | 1030 | 1090 |
| Beryllium | 17.2 | 18.4 |
| Boron | 243 | 243 |
| Cadmium | 53.1 | 55.2 |
| Calcium (%) | 1.45 | 1.47 |
| Chromium | 141 | 145 |
| Cobalt | 37.3 | 39.9 |
| Copper | 708 | 732 |
| Iron (%) | 15.3 | 15.7 |
| Lead (%) | 3.94 | 3.98 |
| Magnesium | 4030 | 4000 |
| Manganese | 194 | 206 |
| Molybdenum | 701 | 733 |
| Nickel | 796 | 852 |
| Selenium | <4 | <4 |
| Silicon | 860 | 1010 |
| Silver | <0.2 | <0.2 |
| Sodium | 6970 | 6900 |
| Strontium | 29.3 | 30.0 |
| Thallium | <8 | <8 |
| Tin | 80 | 86 |
| Titanium | 85.3 | 84.2 |
| Vanadium | 2390 | 2310 |
| Zinc (%) | 1.46 | 1.48 |

[a] Except as indicated.

### Discussion

Deviations From QA Plan--

For Sites D and G, o-chlorotoluene was substituted for 2,4,5-trichlorophenol. This change was based on a request from the EPA Project Officer that a less toxic compound, not listed in Appendix VIII of the May 19, 1980 Federal Register, be chosen for spiking. Minor changes in instrument operating conditions have been noted in the discussion of analytical procedures contained in Section 5 of this report.

Fuel feed samples analyzed for volatile organics were diluted in tetraglyme (tetraethylene glycol dimethyl ether) rather than the polyethylene glycol specified in the QA plan. Tetraglyme is similar in chemical and physical properties to polyethylene glycol but contains fewer interfering contaminants. All QC data generated for volatiles in fuel samples were obtained using the tetraglyme procedure.

Precision, Accuracy and Completeness--

Precision and accuracy goals presented in the QA plan are averages for a stated analytical category. The precision and accuracy achieved in this program and documented in the data presented here are generally in line with the stated goals. However, an individual compound or element within an analytical category may not meet the stated precision or accuracy objective. When this occurs, the data are reviewed and compared to results achieved in similar analytical programs; if the results are comparable, the data are judged valid.

The quantitative analysis of stack gas on Tenax did not achieve the stated precision and accuracy goals and internal quality control data, presented earlier in this section, indicate that the quantitative results are not reliable. The qualitative results from the Tenax analysis have been judged acceptable.

The data for dibenzofurans and dibenzodioxins in Method 5 train extracts do not achieve the accuracy goals stated in the QA plan. However, based on the consistency of the results the data have been released with the caveat that they be considered minimum values.

Completeness, as defined in the QA plan, is the percentage of all measurements made whose results are judged to be valid. In general, all reported data are considered valid; the exceptions are the Tenax results discussed earlier and the GC/ECD results for o-chlorotoluene. This compound could not be detected by the GC/ECD techniques used in this program; a more detailed discussion is provided in Section 5 of this report.

## PERFORMANCE AND SYSTEM AUDITS

### Sampling and Field Measurements Performance Audits

No GCA performance audits of sampling and field measurements were conducted but the EPA 0982 Method 5 audit was completed during this program. A mean percent difference of 2.4 percent between GCA's reported values and EPA's expected values was achieved for the five dry gas meters checked.

## Laboratory Analysis Performance Audits

Several sets of QC samples prepared at GCA by spiking compounds of interest into an oil matrix served to audit the accuracy of analytical work. Although identified as QC samples, their concentrations were not known to the analyst. Table 56 indicates the table in this section which summarizes results on these samples.

In addition, at GCA's request, EPA provided audit materials specific to this project. These included audit cylinders containing chloroform, trichloroethylene and perchloroethylene to check on the GC/ECD work. Unfortunately, the concentration of these cylinders was too high for quantitation with the electron capture detector. The ECD work was checked with samples made up from NBS-certified permeation tubes. The results are shown in Table 40. GCA sent six Tenax cartridges to EPA for fortifications with volatile organic compounds of interest. Table 43 presents these results.

## System Audit

A system audit is an overall evaluation of a project to check on the use of appropriate QC measures and ensure that the quality system planned for the project has been implemented. Such an audit, incorporating both sampling and field measurements and analytical work was conducted by GCA's QA Manager in July 1983. The summary audit report is presented in this subsection.

TABLE 56. INTERNAL QC SAMPLES SERVING AS PERFORMANCE AUDITS

| Matrix | Spiked Compounds | Results Table |
|---|---|---|
| Waste Oil | Volatile Organics | 6-1 |
| Waste Oil | Semivolatile Organics | 6-3, 6-4, 6-5 |
| Mineral Oil | Chlorobenzene | 6-11 |
| Method 5 Filters/XAD | Semivolatile Organics | 6-18 |
| NBS Urban Dust (SRM 1649) | Organics (Polynuclear Aromatics) | 6-20 |
| Method 5 Filter | Metals | 6-22 |
| NBS Urban Particulates (SRM 1648) | Trace Elements | 6-21 |
| NBS Coal Fly Ash (SRM 1633) | Trace Elements | 6-23 |
| NaOH Impinger Solutions | Chloride | 6-25 |

GCA Technology Division

213 Burlington Road
Bedford, Mass. 01730
(617) 275-5444

To: 1-619-068, 1-619-088 Files

Date: 12 August 1983

From: RoseMary Ellersick

Subject: QA Audit - Environmental Characterization of Disposal of Waste Oils through Combustion

These projects deal with measuring emissions resulting from the combustion of waste lubricating oils in small boilers; the QA Project Plan prepared for 1-619-068 applies to both work assignments. A system audit conducted during the week of July 25, 1983 checked on the use of the QC measures outlined in the June 30, 1983 Revised Test/QA Plan.

Monthly reports and the project files of the field measurements and laboratory analysis principal investigators were reviewed during the audit. The field measurements investigator maintained a bound notebook with dated entries documenting project meetings and phone calls and decisions reached, as well as calculations, spiking compounds and concentrations, and sampling site data. He kept a ring-binder for each site with separate sections for each type of analytical data and each set of test run data. The laboratory principal investigator also maintained a project ring-binder classified according to type of analyses.

Site A data was reviewed by the auditor for adherence to the QA Plan; calculations and transcription of raw data to the Site A Draft Data Summary Report were spot-checked. Lab/Field Coordination Forms and the appropriate field data sheets were used. Samples were identified with the alphanumeric codes presented in the QA Plan and a spot-check of a custody form with the Sample Bank Master Log showed agreement.

Calculations of the spiked volatile organic compound concentrations in the diluted waste oil used for the last three runs at Site A were checked and found to be correct. Field project team notebooks showed clear, dated entries; calibration data sheets for the DuPont pumps used to collect Tedlar bag samples were included. Spot-checks on Site A samples showed calibrated flowrates were correctly entered and total volumes sampled were calculated accurately.

Raw data from the analysis of fuel oil for volatile organic compounds was checked for the inclusion of specified QC samples and spot-checked for accuracy of calculations and data transcription. Site A samples were extracted into tetraglyme and analyzed by GC/MS purge and trap techniques on February 24 and 25, 1983. Standards were made up in tetraglyme and a five-point calibration curve was run on February 22. Three blind QC samples were prepared from a background oil, carried through the tetraglyme extraction and analyzed on February 23. These QC samples validated both the calibration standards and the overall method. On each analysis day, a laboratory control sample (a QC sample whose true value is known to the analyst) and a tetraglyme blank were analyzed to document instrument response and the absence of contamination, and to check the calibration curve before any project samples were run. Three aliquots of one Site A fuel sample were analyzed to estimate analytical precision. Relative standard deviations for the four spiked volatile compounds ranged from 12-17%.

Some confusion over the identification of the sample analyzed in triplicate was investigated. The auditor checked notebook pages and GC/MS computer printouts and confirmed that the sample run in triplicate was GCA #29466. The disk File Record Numbers on the printouts and the instrument log were also checked to ensure identification was correct; the data is correctly reported in the Analytical QC report.

Laboratory notebook pages and computer printouts were checked for calculations. Weights and concentrations of standards were checked as were the weights of fuel oil samples extracted into tetraglyme. The calculation of concentration of volatile organics in the fuel from the instrument printout of concentration in the purge solution was spot-checked for each Site A field and QC sample. The only error found in the raw data was corrected in the analytical report.

Two minor deviations from the Test/QA Plan were found. Continuous monitors were used to measure $O_2$ and CO and a Fyrite analyzer was used to measure $CO_2$ instead of Orsat analyzer measurements of these gases. For the extraction of volatile organic compounds from the waste oil feeds, tetraglyme was used instead of polyethylene glycol. In the auditor's opinion, neither of these changes have any negative impact on the quality of the data.

This audit demonstrated that the QC measures outlined in the Test/QA Plan had been conscientiously applied by the project team.

RoseMary Ellersick

RoseMary Ellersick
QA Manager

RME/cf

cc: M.L. Atkinson
T.R. Copeland
P.F. Fennelly
R.R. Hall
T.G. Hopper
M.M. McCabe
L.M. Seale

## QUALITY PROBLEMS AND CORRECTIVE ACTIONS

GCA's quality program emphasizes the use of appropriate immediate corrective actions to prevent the collection of invalid data. Internal QC checks include acceptance limits and planned corrective actions whenever possible so that field samplers and analysts can detect the need for corrective action and implement it. When this can be done, notations are made in field or laboratory notebooks but no other documentations is necessary. Problems which cannot be solved by on-the-spot actions are documented on Corrective Action (CA) Forms. Two CA forms were initiated for this program.

CA023 was initiated on October 29, 1982 to deal with apparent Tenax contamination problems in the VOST train. Corrective action included collecting duplicate Tedlar bag samples at each site and analyzing the samples by direction injection into a GC/ECD. In addition, duplicate samples from each Tedlar bag were collected on Tenax cartridges with Tenax/Charcoal backup cartridges. The direct injection GC/ECD results proved more precise and reasonable at the first three sites and drawing samples from the bags over the sorbent cartridges was discontinued. The problem was resolved for this program; the VOST train was to be eliminated from the program. However, to provide more data on use of the train in a relatively clean environment, GCA ran multiple VOST trains during the six test runs at Site D. Results are presented earlier in this report.

The second CA Form (CA033) was initiated on July 26, 1983 because the analysis results on oil samples which were Parr-bombed and then analyzed for chloride by ion chromatography appeared unreasonable. Reanalysis of six samples gave different and more reasonable values; all involved oil samples were reanalyzed. Reanalysis values checked with expected spiked values; this problem is considered solved.

A corrective action which should have been documented on a CA Form but was not was the decision to change the analytical protocol for semivolatile organic compounds in oil from GC/MS to GC/ECD. The action was based on internal QC results and is documented in the files of the laboratory principal investigator and the QC Coordinator.

# APPENDIX A

# SITE DATA SUMMARIES

Site: A

Service: Heat for Office Building

Boiler Type: Smith Mills, Cast Iron

Rated Capacity ($10^6$ Btu/hr): 0.5

Atomization Method: Mechanical

Stack Height (ft): 16

Stack Diameter (ft): 0.83

TABLE 1. WASTE OIL INCINERATION TESTS: SITE A - FLUE GAS DATA

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Fuel feed (gal/hr) | 3.44 | 3.22 | 3.22 | 3.09 | 3.10 | 3.28 |
| Stack T (°F) | 388 | 328 | 392 | 365 | 299 | 370 |
| Volumetric flow rate (dscm/hr) | 406.0 | 381.7 | 373.2 | 367.0 | 393.5 | 370.9 |
| Moisture content (percent) | 4.8 | 4.9 | 6.6 | 7.8 | 6.0 | 5.5 |
| $O_2$ (percent) | 12.0 | 9.6 | 8.0 | 8.5 | 9.2 | 9.6 |
| $CO_2$ (percent) | 5.2 | 7.12 | 7.0 | 7.9 | 7.4 | 7.2 |
| CO (ppm) | 880 | 100 | 60 | 80 | 120 | 80 |
| Excess Air | 121.47 | 77.24 | 55.40 | 62.59 | 71.46 | 77.34 |
| Particulate collected (mg) | 74.5 | 59.3 | 64.0 | 76.6 | 49.3 | 88.0 |
| Particulate emissions (lb/hr) | 0.07 | 0.07 | 0.08 | 0.09 | 0.05 | 0.08 |

TABLE 2. WASTE OIL INCINERATION TESTS: SITE A

| | Results of oil analysis (µg/g) | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| **Volatiles** | | | | | | |
| Chloroform | 1000 | 1100 | 700 | 2000 | 5100 | 2700 |
| Trichloroethane | 1300 | 1400 | 1000 | 2200 | 4600 | 2600 |
| Trichloroethylene | 1200 | 1200 | 800 | 2100 | 4200 | 3000 |
| Tetrachloroethylene | 1800 | 1600 | 1500 | 3500 | 6300 | 5100 |
| **Semivolatiles** | | | | | | |
| Trichlorobenzene | 1000 | 1000 | 960 | 1700 | 3200 | 1600 |
| 1-chloronaphthalene | 1200 | 1200 | 1000 | 1200 | 2500 | 1800 |
| Trichlorophenol | 620 | 830 | 690 | 1100 | 3100 | 2500 |
| **Inorganic components** | | | | | | |
| Chlorine | 4900 | 5270 | 3430 | 9222 | 20200 | 13500 |
| Arsenic | 1.7 | 2.4 | 1.9 | 4.2 | 3.2 | 3.8 |
| Cadmium | 0.9 | 0.9 | 0.9 | 1.1 | 0.9 | 1.0 |
| Chromium | 2.8 | 2.7 | 2.7 | 4.1 | 3.2 | 3.9 |
| Lead | 601 | 615 | 620 | 785 | 620 | 703 |
| Zinc | 287 | 294 | 300 | 375 | 300 | 339 |

## TABLE 3. WASTE OIL INCINERATION TESTS: SITE A

| Organic components | Results of flue gas analysis ($\mu g/m^3$) 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **Volatiles** | | | | | | |
| Chloroform | 150 | 105 | 190 | 30[a] | 55 | 150 |
| Trichloroethane | 50 | 95 | 210 | 30[a] | 70 | 70 |
| Trichloroethylene | 85 | 30[a] | 655 | 30[a] | 115 | 54 |
| Tetrachloroethylene | 530 | 110 | 80 | 30[a] | 205 | 50 |
| **Semivolatiles** | | | | | | |
| Trichlorobenzene | 201 | 16 | ND | ND | - | 9.4 |
| 1-chloronaphthalene | 48 | 9 | ND | ND | - | ND |
| Trichlorophenol | 12 | ND | ND | ND | - | ND |
| Phenol[b] | 730 | | | | | |
| Phenanthrene | 101 | 13 | | | | |
| Phenanthrene, methyl isomers | 38 | | | | | |
| Naphthalene[b,c] | 530 | 78 | 32 | 42 | | |
| Naphthalene, methyl isomers[c] | 50 | 20 | 23 | 34 | | |
| Naphthalene, dimethyl/ethyl isomers[c] | 20 | 20 | | 28 | | |
| Benzaldehyde[c] | 56 | | | | | |
| Benzaldehyde, hydroxy isomers[c] | 27 | | | | | |
| Benzaldehyde, methyl isomers[c] | 37 | | | | | |
| Benzene, alkyl, $C_9H_{12}$ isomers[c] | 6.2 | 59 | 127 | | | |
| Benzene, alkyl, $C_{10}H_{12}$ isomers[c] | 34 | 103 | 61 | 45 | | |
| Benzoic acid[c] | 340 | 88 | 59 | 57 | | 143 |
| Dodecanoic acid | 220 | | 310 | | | |
| 1,1'-Biphenyl | 13 | | | | | |
| Toluene, chloro isomers[b] | 9.0 | | | | | |
| Cinnoline | 35 | | | | | |
| Benzofuran | 83 | | | | | |
| Dibenzofuran | 93 | | | 10 | | |
| 1,3-Isobenzofurandione | 7.9 | | | | | |
| 1,4-Naphthalenedione | 2.4 | | | | | |
| Ethanone, 1-(naphthalonyl) isomers | 51 | | | | | |
| 2H-1-Benzopyran-2-one | 73 | | | | | |
| Dibenzothiophene | 30 | | | | | |
| 1H,3H-Naphtha(1,8-cd)pyran-1,3-dione | 17 | | | | | |
| **Inorganic components** | | | | | | |
| **ICAP Analysis** | | | | | | |
| Arsenic | | | | | 11.2 | |
| Cadmium | | | | | 31.2 | |
| Chromium | | | | | 62.2 | |
| Lead | | | | | 9,680 | |
| Zinc | | | | | 5,150 | |
| **Ion Chromatograph Analysis** | | | | | | |
| HCl | | | | | 400,000 | |

ND = <9.0 $\mu g/m^3$

[a] Trace amount quantified to one significant digit.

[b] Appendix VIII compound.

[c] Component is a known contaminant of XAD resin and/or may be formed during the exposure of resin to combustion source flue gases.

TABLE 4. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS: SITE A

| Component | µg/m³ | | | | | Detection Limit (ND = ) |
|---|---|---|---|---|---|---|
| | Run | | | | | |
| | 1 | 2 | 3 | 4 | 6 | |
| dibenzofuran | 201[a] | 70 | 11 | 23 | 4.3 | 0.08 |
| chlorodibenzofurans | 1.4 | 1.1 | ND | ND | .21 | 0.05 |
| dichlorodibenzofurans | ND | ND | ND | 2.2 | 1.6 | 0.08 |
| trichlorodibenzofurans | ND | ND | ND | ND | ND | 0.08 |
| tetrachlorodibenzofurans | ND | ND | ND | ND | ND | 0.10 |
| pentachlorodibenzofurans | ND | ND | ND | ND | ND | 0.22 |
| hexachlorodibenzofurans | ND | ND | ND | ND | ND | 0.22 |
| heptachlorodibenzofurans | ND | ND | ND | ND | ND | 0.62 |
| octachlorodibenzofurans | ND | ND | ND | ND | ND | 3.1 |
| dibenzodioxin | 1.7 | ND | 1.3 | ND | 0.8 | 0.8 |
| chlorodibenzodioxins | ND | ND | ND | ND | ND | 0.05 |
| dichlorodibenzodioxins | ND | ND | ND | ND | ND | 0.08 |
| trichlorodibenzodioxins | ND | ND | ND | ND | ND | 0.08 |
| tetrachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.10 |
| pentachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.22 |
| hexachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.22 |
| heptachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.62 |
| octachlorodibenzodioxins | ND | ND | ND | ND | ND | 3.1 |

[a] The high level of this component saturated the mass spectrometer during analysis. Accurate quantitation is therefore not possible.

### TABLE 5. WASTE OIL INCINERATION TESTS: SITE A

| Organic components | Destruction and removal efficiencies (percent) | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| **Volatile components** | | | | | | |
| Chloroform | 99.48 | 99.66 | 99.07 | 99.95 | 99.96 | 99.81 |
| Trichloroethane | 99.86 | 99.76 | 99.28 | 99.95 | 99.94 | 99.91 |
| Trichloroethylene | 99.75 | 99.91 | 97.18 | 99.95 | 99.90 | 99.94 |
| Tetrachloroethylene | 98.97 | 99.76 | 99.88 | 99.97 | 99.88 | 99.97 |
| **Semivolatiles** | | | | | | |
| Trichlorobenzene | 99.30 | 99.94 | >99.98 | >99.99 | ----- | 99.98 |
| 1-chloronaphthalene | 99.86 | 99.97 | >99.98 | >99.98 | ----- | >99.98 |
| Trichlorophenol | 99.43 | >99.97 | >99.97 | >99.99 | ----- | >99.99 |

Site: C

Service: Heat and Process Steam for Greenhouse Complex

Boiler Type: Eureka, Horizontal Return Tube

Rated Capacity ($10^6$ Btu/hr): 2.4

Atomization Method: Rotary Cup

Stack Height (ft): 20

Stack Diameter (ft): 1.25

TABLE 1. WASTE OIL INCINERATION TESTS: SITE C--FLUE GAS DATA

| | 1 | 2 | 3 |
|---|---|---|---|
| Fuel feed (gal/hr) | 25.55 | 23.27 | 23.33 |
| Stack T (°F) | 440 | 430 | 441 |
| Volumetric flow rate (dscm/hr) | 1514.7 | 1514.1 | 1598.9 |
| Moisture content (percent) | 7.9 | 7.8 | 7.8 |
| $O_2$ (percent) | 10.0 | 9.8 | 10.3 |
| $CO_2$ (percent) | 7.5 | 7.4 | 6.6 |
| CO (ppm) | 100 | 20 | 20 |
| Particulate collected (mg) | 413.2 | 333.8 | 347.1 |
| Excess Air | 84.19 | 81.40 | 87.94 |
| Particulate emissions (lb/hr) | 1.40 | 1.08 | 1.12 |

TABLE 2. WASTE OIL INCINERATION TESTS: SITE C

| Organic components | Results of oil analysis (μg/g) 1 | 2 | 3 |
|---|---|---|---|
| **Volatiles** | | | |
| Chloroform | 2400 | 2500 | 2600 |
| Trichloroethane | 3200 | 3000 | 3400 |
| Trichloroethylene | 2200 | 2200 | 2700 |
| Tetrachloroethylene | 4200 | 4000 | 4200 |
| **Semivolatiles** | | | |
| Trichlorobenzene | 2600 | 2600 | 2300 |
| 1-chloronaphthalene | 1900 | 1800 | 2000 |
| Trichlorophenol | 850 | 1200 | 2400 |
| **Inorganic Components** | | | |
| Chlorine | 13100 | 11700 | 12000 |
| Arsenic | 8.9 | 9.4 | 8.7 |
| Cadmium | 0.9 | 1.1 | ND |
| Chromium | 8.3 | 8.5 | 8.1 |
| Lead | 1640 | 1650 | 1570 |
| Zinc | 806 | 837 | 820 |

ND = <0.2 μg/g

## TABLE 3. WASTE OIL INCINERATION TESTS: SITE C

| Organic compounds | Results of flue gas analysis (µg/$m^3$) | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| **Volatiles** | | | |
| Chloroform | 100 | 105 | 140 |
| Trichloroethane | 95 | 75 | 95 |
| Trichloroethylene | 77 | 110 | 95 |
| Tetrachloroethylene | 225 | 195 | 185 |
| **Semivolatiles** | | | |
| Trichlorobenzene | - | 21 | 18 |
| 1-chloronaphthalene | - | 11 | 13 |
| Trichlorophenol | - | ND | 9.0 |
| Bis (2 ethyl hexyl) phthalate[a] | - | 2,237 | 918 |
| Napthalene[a,b] | - | 27 | 22 |
| Benzene, tetrachloro isomers[a] | - | 19 | 19 |
| Benzene, alkyl $C_9H_{12}$ isomers[b] | - | - | 39 |
| Benzene, alkyl, $C_{10}H_{14}$ isomers[b] | - | 13 | 15 |
| **Inorganic Components** | | | |
| **ICAP Analysis** | | | |
| Arsenic | 655 | | |
| Cadmium | 102 | | |
| Chromium | 166 | | |
| Lead | 72,400 | | |
| Zinc | 33,700 | | |
| **Ion Chromatograph Analysis** | | | |
| HCl | 358,100 | | |

ND = <6 µg/$m^3$

[a] Appendix VIII compounds

[b] Component is a known contaminant of XAD resin and/or may be formed during the exposure of resin to combustion source flue gases.

TABLE 4. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS: SITE C

| | $\mu g/m^3$ | | |
|---|---|---|---|
| | Run | | |
| Component | 2 | 3 | Detection Limit (ND = ) |
| dibenzofuran | 6.7 | 4.2 | 0.05 |
| chlorodibenzofurans | ND | 0.52 | 0.03 |
| dichlorodibenzofurans | ND | 0.07 | 0.05 |
| trichlorodibenzofurans | 0.86 | 0.10 | 0.05 |
| tetrachlorodibenzofurans | ND | ND | 0.06 |
| pentachlorodibenzofurans | ND | ND | 0.14 |
| hexachlorodibenzofurans | ND | ND | 0.14 |
| heptachlorodibenzofurans | ND | ND | 0.40 |
| octachlorodibenzofurans | ND | ND | 2.0 |
| dibenzodioxin | ND | ND | 0.05 |
| chlorodibenzodioxins | ND | 0.27 | 0.03 |
| dichlorodibenzodioxins | ND | 0.18 | 0.05 |
| trichlorodibenzodioxins | ND | ND | 0.05 |
| tetrachlorodibenzodioxins | ND | ND | 0.06 |
| pentachlorodibenzodioxins | ND | ND | 0.14 |
| hexachlorodibenzodioxins | ND | ND | 0.14 |
| heptachlorodibenzodioxins | ND | ND | 0.40 |
| octachlorodibenzodioxins | 4.5 | ND | 2.0 |

TABLE 5. WASTE OIL INCINERATION TESTS: SITE C

| Organic components | Destruction and removal efficiencies (percent) | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Volatile Components | | | |
| Chloroform | 99.93 | 99.92 | 99.89 |
| Trichloroethane | 99.95 | 99.95 | 99.94 |
| Trichloroethylene | 99.94 | 99.90 | 99.93 |
| Tetrachloroethylene | 99.90 | 99.91 | 99.91 |
| Semivolatiles | | | |
| Trichlorobenzene | - | 99.98 | 99.98 |
| 1-chloronaphthalene | - | 99.99 | 99.99 |
| Trichlorophenol | - | >99.99 | 99.99 |

Site: D

Service: Heat for an Office Building Complex

Boiler Type: York Shipley, Three Pass Scotch Firetube

Rated Capacity ($10^6$ Btu/hr): 2.4

Atomization Method: Air

Stack Height (ft): 30

Stack Diameter (ft): 1.25

TABLE 1. WASTE OIL INCINERATION TESTS: SITE D - FLUE GAS DATA

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Fuel feed (gal/hr) | 13.13 | 12.71 | 13.12 | 13.67 | 13.67 | 12.56 |
| Stack T (°F) | 220 | 237 | 236 | 293 | 239 | 283 |
| Volumetric flow rate (dscm/hr) | 1828.7 | 1434.4 | 1416.9 | 1324.7 | 1449.7 | 1421.2 |
| Moisture content (percent) | 3.1 | 6.4 | 6.3 | 8.2 | 7.7 | 9.4 |
| $O_2$ (percent) | 13.5 | 13.2 | 12.0 | 12.0 | 12.0 | 12.0 |
| $CO_2$ (percent) | 5.5 | 5.4 | 5.5 | 5.0 | 5.5 | 5.5 |
| CO (ppm) | 350 | 350 | 350 | 350 | 340 | 340 |
| Excess Air | 167 | 153 | 113 | 112 | 113 | 113 |
| Particulate collected (mg) | 216.5 | 166.9 | 152.6 | 213.0 | 112.8 | 85.9 |
| Particulate emissions (lb/hr) | 0.54 | 0.64 | 0.58 | 0.91 | 0.43 | 0.55 |

## TABLE 2. WASTE OIL INCINERATION TESTS: SITE D

| | Results of oil analysis (µg/g) | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| **Volatiles** | | | | | | |
| Chloroform | 2300 | 2500 | 2400 | 8600 | 9100 | 8900 |
| Trichloroethane | 2600 | 3000 | 3000 | -- | -- | -- |
| Trichloroethylene | 2300 | 2000 | 1900 | -- | -- | -- |
| Tetrachloroethylene | 3400 | 2900 | 2200 | 7700 | 7800 | 8500 |
| **Semivolatiles** | | | | | | |
| Trichlorobenzene | 2000 | 1800 | 1800 | 5300 | 5900 | 6200 |
| 1-chloronaphthalene | 1600 | 1400 | 1500 | -- | -- | -- |
| **Inorganic components** | | | | | | |
| Chlorine | 12100 | 11300 | 11200 | 20800 | 21300 | 20700 |
| Arsenic | 2.4 | 2.3 | 2.3 | 3.3 | 3.1 | 3.2 |
| Cadmium | 1.09 | 1.09 | 1.10 | 1.31 | 1.39 | 1.38 |
| Chromium | 4.05 | 4.05 | 4.15 | 4.83 | 4.83 | 5.02 |
| Lead | 724 | 755 | 761 | 915 | 919 | 919 |
| Zinc | 366 | 381 | 385 | 457 | 464 | 465 |

## TABLE 3. WASTE OIL INCINERATION TESTS: SITE D

| Organic components | Results of flue gas analysis ($\mu g/m^3$) 1 | 2 | 3 | 4 | 5 | 6 | Background test |
|---|---|---|---|---|---|---|---|
| **Volatiles** | | | | | | | |
| Chloroform | 43 | 30[a] | 30[a] | 30[a] | 20[a] | 115 | NA |
| Trichloroethane | 37 | 10[a] | 20[a] | -- | -- | -- | NA |
| Trichloroethylene | 78 | 74 | 47 | -- | -- | -- | NA |
| Tetrachloroethylene | 150 | 250 | 97 | 130 | 150 | 305 | NA |
| Trichlorofluoromethane | 50 | 30 | 50 | 80 | -- | 15 | NA |
| Trichloropropanaic acid | 22 | -- | -- | -- | -- | -- | NA |
| Hexane | 190 | -- | 40 | -- | -- | -- | NA |
| Cyclohexane | 80 | -- | 40 | -- | -- | -- | NA |
| Methyl cyclohexane | 110 | -- | -- | -- | -- | -- | NA |
| Butanol | -- | 20 | -- | -- | -- | -- | NA |
| Dimethylcyclopentadiene isomers | -- | -- | -- | -- | 50 | 45 | NA |
| Benzene | 150 | 24 | -- | 20 | -- | 20 | NA |
| Toluene | 240 | 110 | -- | 15 | -- | 30 | NA |
| **Semivolatiles** | | | | | | | |
| Trichlorobenzene | -- | 107 | 50 | 67 | 42 | 98 | |
| 1-chloronaphthalene | -- | 27 | 17 | -- | -- | -- | |
| Chlorotoluene | | 12 | ND | | | | 13 |
| Naphthalene[b,c] | -- | 72 | | | | | |
| Napththalene, methyl isomers[c] | -- | 18 | | | | | |
| Naphthalene, dimethyl/ethyl isomers[c] | -- | 6 | | | 7 | | |
| Benzaldehyde, 5-(chlroemethyl)-2hydroxy | | | 25 | | 25 | 68 | |
| Benzaldehyde, hydroxy isomers[c] | | | | | | | |
| Benzaldehyde, methyl isomers[c] | | | | | | | |
| Benzene, alkyl, $C_9H_{12}$ isomers[c] | | | 4.2 | | | 17 | |
| Benzene, alkyl, $C_{10}H_{14}$ isomers[c] | | 116 | 18 | | 14 | 34 | |
| Benzoic acid[c] | | 210 | 24 | 64 | 66 | 137 | |
| Benzoic acid, dimethyl isomers[c] | | 84 | 37 | 57 | 34 | 22 | |
| Toluene, chloro isomers[b] | | 68 | | | | | |
| Dibenzofuran | | | 2.3 | | | | |
| Benzene, ethynyl[c] | | 18 | 7.0 | 2.4 | 1.6 | 4.0 | |
| Benzene, ethenyl[c] | | 18 | 7.3 | 2.4 | 3.9 | 4.3 | |
| Ethanone, 1-phenyl[c] | | | | | 13 | 16 | |
| Ethanone, dimethyl phenyl isomers[c] | | | 5.0 | | | 14 | |
| Diethylphthalate | | | | | | | 71 |
| Bis(2 ethyl hexyl)phthalate | | | | | | | 205 |
| P-chloro-m-cresol | | | | | | | 17 |
| **Inorganic components** | | | | | | | |
| **ICAP Analysis** | | | | | | | |
| Arsenic | 26.1 | | | | | | 22.1 |
| Cadmium | 8.3 | | | | | | <0.7 |
| Chromium | 111.8 | | | | | | 29.3 |
| Lead | 5388 | | | | | | 243 |
| Zinc | 3134 | | | | | | 206 |
| **Ion Chromatograph Analysis** | | | | | | | |
| HCl | 184,000 | | | | | | 2240 |

ND = <9.0 $\mu g/m^3$

[a] Trace amount quantified to one significant digit.

[b] Appendix VIII Compound.

[c] Component is a known contaminant of XAD resin and/or may be formed during the exposure of resin to combustion source flue gases.

TABLE 4. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS: SITE D

| Component | µg/m³ |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | Run |  |  |  |  |  |  |
|  | 1 | 2 | 3 | 4 | 6 | Detection Limit (ND = ) |  |
| dibenzofuran | 5.6 | 6.8 | 2.0 | 1.5 | 1.3 |  | 0.10 |
| chlorodibenzofurans | ND | 1.8 | 0.14 | 0.14 | ND | 0.03 | 0.06 |
| dichlorodibenzofurans | ND | ND | ND | ND | ND | 0.05 | 0.10 |
| trichlorodibenzofurans | ND | ND | ND | ND | ND | 0.05 | 0.10 |
| tetrachlorodibenzofurans | ND | ND | ND | ND | ND | 0.06 | 0.12 |
| pentachlorodibenzofurans | ND | ND | ND | ND | ND | 0.14 | 0.30 |
| hexachlorodibenzofurans | ND | ND | ND | ND | ND | 0.14 | 0.30 |
| heptachlorodibenzofurans | ND | ND | ND | ND | ND | 0.40 | 0.80 |
| octachlorodibenzofurans | ND | ND | ND | ND | ND | 2.0 | 4.0 |
| dibenzodioxin | ND | ND | ND | ND | ND | 0.05 | 0.10 |
| chlorodibenzodioxins | ND | ND | ND | ND | ND | 0.03 | 0.06 |
| dichlorodibenzodioxins | ND | ND | ND | ND | ND | 0.05 | 0.10 |
| trichlorodibenzodioxins | ND | ND | ND | ND | ND | 0.05 | 0.10 |
| tetrachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.06 | 0.12 |
| pentachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.14 | 0.30 |
| hexachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.14 | 0.30 |
| heptachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.40 | 0.80 |
| octachlorodibenzodioxins | ND | ND | ND | ND | ND | 2.0 | 4.0 |

## TABLE 5. WASTE OIL INCINERATION TESTS: SITE D

| | Destruction and removal efficiences (percent) | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Volatile components | | | | | | |
| Chloroform | 99.92 | 99.96 | 99.96 | 99.99 | 99.99 | 99.96 |
| Trichloroethane | 99.94 | 99.99 | 99.98 | -- | -- | -- |
| Trichloroethylene | 99.86 | 99.88 | 99.92 | -- | -- | -- |
| Tetrachloroethylene | 99.81 | 99.72 | 99.86 | 99.95 | 99.95 | 99.88 |
| Semivolatiles | | | | | | |
| Trichlorobenzene | -- | 99.98 | 99.91 | 99.96 | 99.98 | 99.95 |
| 1-chloronaphthalene | -- | 99.94 | 99.96 | -- | -- | -- |

Site: E

Service: Heat and Process Steam for a Greenhouse Complex

Boiler Type: Preferred, Four Pass Firetube

Rated Capacity ($10^6$ Btu/hr): 3.4

Atomization Method: Rotary Cup

Stack Height (ft): 80

Stack Diameter (ft): 1.25

## TABLE 1. WASTE OIL INCINERATION TESTS: SITE E FLUE GAS DATA

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Fuel feed (gal/hr) | 16.20 | 14.97 | 16.81 | 15.99 | 15.04 | 14.95 | 13.12 | 12.50 | 11.48 |
| Stack T (°F) | 191 | 195 | 189 | 198 | 203 | 198 | 202 | 208 | 210 |
| Volumetric flow rate (dscm/hr) | 2388.6 | 2390.9 | 2329.0 | 2382.1 | 2208.4 | 2220.3 | 2407.8 | 2361.9 | 2389.3 |
| Moisture content (percent) | 5.4 | 2.1 | 5.7 | 5.3 | 5.0 | 4.6 | 5.2 | 5.2 | 5.2 |
| $O_2$ (percent) | 16.0 | 16.1 | 15.6 | 15.6 | 15.5 | 160 | 18.5 | 18.7 | 19.9 |
| $CO_2$ (percent) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 1.0 | 1.0 | 1.0 |
| CO (ppm) | ND | ND | ND | ND | ND | ND | 20 | 25 | 40 |
| Excess Air | 259.07 | 266.13 | 233.48 | 233.48 | 227.67 | 183.52 | -- | -- | -- |
| Particulate collected (mg) | 151 | 125 | 139 | 130 | 101 | 94 | -- | -- | -- |
| Particulate emissions (lb/hr) | 0.80 | 0.67 | 0.72 | 0.71 | 0.53 | 0.70 | -- | -- | -- |

ND = <10 ppm

## TABLE 2. WASTE OIL INCINERATION TESTS: SITE E

| Organic components | Results of oil analysis (μg/g) 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| **Volatiles** | | | | | | | | | |
| Chloroform | 2700 | 2900 | 2000 | ----- | ----- | ----- | 8050 | 3050 | 3400 |
| Trichloroethane | 2900 | 3200 | 3300 | ----- | ----- | ----- | 12500 | 6000 | 5800 |
| Trichloroethylene | 3500 | 2800 | 2300 | ----- | ----- | ----- | ND | ND | ND |
| Tetrachloroethylene | 3900 | 2800 | 3500 | ----- | ----- | ----- | 9350 | 3600 | 3900 |
| **Semi-Volatiles** | | | | | | | | | |
| Trichlorobenzene | 2600 | 1900 | 2600 | 2600 | 3000 | 2600 | ---- | ---- | ---- |
| 1-chloronaphthalene | 2400 | 2400 | 2200 | 3500 | 2300 | 1800 | ---- | ---- | ---- |
| Trichlorophenol | 600 | 630 | 900 | 880 | 390 | 1200 | ---- | ---- | ---- |
| **Inorganic components** | | | | | | | | | |
| **ICAP Analysis** | | | | | | | | | |
| Chlorine | 13300 | 13500 | 12000 | 19400 | 18500 | 18600 | ---- | ---- | ---- |
| Arsenic | 11.0 | 11.0 | 10.5 | 9.9 | 10.4 | 10.8 | ---- | ---- | ---- |
| Cadmium | 1.6 | 1.8 | 1.1 | 2.0 | 1.6 | 1.2 | ---- | ---- | ---- |
| Chromium | 8.0 | 8.3 | 7.9 | 7.8 | 7.7 | 8.0 | ---- | ---- | ---- |
| Lead | 1550 | 1550 | 1560 | 1470 | 1550 | 1530 | ---- | ---- | ---- |
| Zinc | 762 | 773 | 774 | 675 | 768 | 764 | ---- | ---- | ---- |

## TABLE 3. WASTE OIL INCINERATION TESTS: SITE E

| Organic components | Results of flue gas analysis (µg/M³) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| **Volatiles** | | | | | | | | | |
| Chloroform | 31.0 | 155 | 40.0 | ---- | ---- | ---- | 30[a] | 30[a] | 30[a] |
| Trichloroethane | 703 | 404 | 718 | ---- | ---- | ---- | 685 | 530 | 460 |
| Trichloroethylene | 57.5 | 158 | 64.5 | ---- | ---- | ---- | ---- | ---- | ---- |
| Tetrachloroethylene | 196 | 200 | 195 | ---- | ---- | ---- | 350 | 220 | 180 |
| **Semi-Volatiles** | | | | | | | | | |
| Trichlorobenzene | ---- | 17.6 | 11.2 | 9.5 | 6.7 | 230.1 | ---- | ---- | ---- |
| 1-chloronaphthalene | ---- | 12.4 | ND | ND | ND | 86 | ---- | ---- | ---- |
| Trichlorophenol | ---- | ND | ND | ND | ND | 55 | ---- | ---- | ---- |
| Phenol[b] | ---- | 13 | 8.3 | ---- | 17 | 26 | ---- | ---- | ---- |
| Phenanthrene | ---- | ---- | 1.8 | ---- | ---- | ---- | ---- | ---- | ---- |
| 1,2 Dichlorobenzene[b] | ---- | ---- | ---- | ---- | ---- | 5.4 | ---- | ---- | ---- |
| 1,3/1,4-Dichlorobenzene[b] | ---- | ---- | ---- | ---- | ---- | 5.5 | ---- | ---- | ---- |
| Benzene, chloromethyl | ---- | --- | 9.2 | ---- | 8 | ---- | ---- | ---- | ---- |
| Napthalene[b,c] | ---- | 14 | 12 | 11 | 9.3 | 9 | ---- | ---- | ---- |
| Benzene, dimethyl, isomers[c] | ---- | 12 | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Benzene, alkyl $C_8H_{10}$ isomers[c] | ---- | ---- | 14 | 11 | 6 | 51 | ---- | ---- | ---- |
| Benzene, alkyl $C_9H_{12}$ isomers[c] | ---- | 75 | 140 | 140 | 45 | 553 | ---- | ---- | ---- |
| Benzene, alkyl, $C_{10}H_{14}$ isomers[c] | ---- | 33 | 50 | 34 | 28 | ---- | ---- | ---- | ---- |
| Benzaldehyde, alkyl isomers[c] | ---- | 32 | 26 | ---- | ---- | 154 | ---- | ---- | ---- |
| Benzoic acid[c] | ---- | 250 | 110 | ---- | 160 | 246 | ---- | ---- | ---- |
| Napthalene, methyl isomers[c] | ---- | 14 | 14 | 17 | ---- | 34 | ---- | ---- | ---- |
| **Inorganic components** | | | | | | | | | |
| **ICAP Analysis** | | | | | | | | | |
| Arsenic | 106 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Cadmium | 182 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Chromium | 230 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Lead | 20300 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Zinc | 12100 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| **Ion Chromatograph Analysis** | | | | | | | | | |
| HCl | 440000 | | | | | | | | |

ND = <6 µg/m³

[a] Trace amount quantified to one significant digit.

[b] Appendix VIII compound.

[c] Component is a known contaminant of XAD resin and/or may be formed during the exposure of resin to combustion source flue gases.

## TABLE 4. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS: SITE E

| Component | $\mu g/m^3$ | | | | | Detection Limit (ND = ) |
|---|---|---|---|---|---|---|
| | Run | | | | | |
| | 2 | 3 | 4 | 5 | 6 | |
| dibenzofuran | 3.8 | 1.1 | 3.4 | 2.3 | 29 | 0.08 |
| chlorodibenzofurans | ND | 0.26 | 0.49 | ND | ND | 0.05 |
| dichlorodibenzofurans | ND | ND | 0.24 | ND | ND | 0.08 |
| trichlorodibenzofurans | ND | ND | ND | ND | ND | 0.08 |
| tetrachlorodibenzofurans | ND | 0.17 | ND | ND | ND | 0.09 |
| pentachlorodibenzofurans | ND | ND | ND | ND | ND | 0.21 |
| hexachlorodibenzofurans | ND | ND | ND | ND | ND | 0.21 |
| heptachlorodibenzofurans | ND | ND | ND | ND | ND | 0.61 |
| octachlorodibenzofurans | ND | ND | ND | ND | ND | 3.1 |
| dibenzodioxin | ND | ND | 0.73 | ND | ND | 0.08 |
| chlorodibenzodioxins | ND | ND | ND | ND | ND | 0.05 |
| dichlorodibenzodioxins | ND | ND | 1.6 | ND | ND | 0.08 |
| trichlorodibenzodioxins | ND | ND | ND | ND | ND | 0.08 |
| tetrachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.09 |
| pentachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.21 |
| hexachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.21 |
| heptachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.61 |
| octachlorodibenzodioxins | ND | ND | ND | ND | ND | 3.1 |

## TABLE 5. WASTE OIL INCINERATION TESTS: SITE E

| Organic components | Destruction and removal efficiencies (percent) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| **Volatile Components** | | | | | | | | | |
| Chloroform | 99.95 | 99.75 | 99.92 | ---- | ---- | ---- | 99.97 | 99.91 | 99.91 |
| Trichloroethane | 98.94 | 99.40 | 99.11 | ---- | ---- | ---- | 99.70 | 99.56 | 99.51 |
| Trichloroethylene | 99.93 | 99.73 | 99.88 | ---- | ---- | ---- | ---- | ---- | ---- |
| Tetrachloroethylene | 99.78 | 99.66 | 99.77 | ---- | ---- | ---- | 99.80 | 99.66 | 99.71 |
| **Semi-Volatiles** | | | | | | | | | |
| Trichlorobenzene | ---- | 99.96 | 99.98 | 99.98 | 99.99 | 99.61 | ---- | ---- | ---- |
| 1-chloronaphthalene | ---- | 99.97 | >99.99 | >99.99 | >99.99 | 99.78 | ---- | ---- | ---- |
| Trichlorophenol | ---- | >99.95 | >99.97 | >99.97 | >99.93 | 99.80 | ---- | ---- | ---- |

Site: F

Service: Heat and Process Steam for Greenhouse Complex

Boiler Type: Ray, Three Pass Firetube Boiler

Rated Capacity ($10^6$ Btu/hr): 4.2

Atomization Method: Air

Stack Height (ft): 80 (common external stack)

Stack Diameter (ft): 1.2 (sampling duct)

## TABLE 1. WASTE OIL INCINERATION TESTS: SITE F FLUE GAS DATA

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Fuel feed (gal/hr) | 17.63 | 14.35 | 20.50 | 26.17 | 27.06 | 23.40 | 31.98 | 27.88 | 19.48 |
| Stack T (°F) | 554 | 539 | 606 | 493 | 480 | 462 | 692 | 688 | 666 |
| Volumetric flow rate (dscm/hr) | 1257.2 | 1311.3 | 1393.2 | 1838.6 | 1726.0 | 1673.0 | 1363.1 | 1309.8 | 1273.5 |
| Moisture content (percent) | 12.3 | 8.3 | 5.4 | 7.3 | 8.3 | 9.6 | 8.5 | 8.5 | 8.5 |
| $O_2$ (percent) | 11.1 | 15.0 | 11.0 | 9.7 | 8.2 | 9.2 | 5.0 | 5.0 | 5.0 |
| $CO_2$ (percent) | 3.6 | 3.4 | 6.9 | 6.9 | 8.2 | 7.4 | 10.5 | 11.0 | 9.0 |
| CO (ppm) | ND | ND | ND | ND | ND | ND | 25 | 30 | 30 |
| Excess Air | 97.20 | 229.27 | 103.05 | 78.75 | 59.12 | 71.78 | -- | -- | -- |
| Particulate collected (mg) | 104.1 | 157.7 | 241.4 | 155.0 | 251.1 | 189.9 | -- | -- | -- |
| Particulate emissions (lb/hr) | 0.38 | 0.61 | 0.92 | 0.88 | 1.01 | 1.06 | -- | -- | -- |

ND = <10 ppm

## TABLE 2. WASTE OIL INCINERATION TESTS: SITE F

| Organic components | Results of oil analysis (µg/g)<br>1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| **Volatiles** | | | | | | | | | |
| Chloroform | ----- | ----- | ----- | 3400 | 4400 | 3700 | 3500 | 1300 | 1200 |
| Trichloroethane | ----- | ----- | ----- | 4200 | 4200 | 3900 | 6300 | 2700 | 2300 |
| Trichloroethylene | ----- | ----- | ----- | 3100 | 3900 | 2800 | ND | ND | ND |
| Tetrachloroethylene | ----- | ----- | ----- | 7700 | 5700 | 3500 | 5300 | 1200 | 740 |
| **Semi-Volatiles** | | | | | | | | | |
| Trichlorobenzene | 1800 | 1800 | 3100 | 2900 | 2700 | 2400 | ---- | ---- | ---- |
| 1-chloronaphthalene | 2900 | 2700 | 2800 | 5200 | 3600 | 2400 | ---- | ---- | ---- |
| Trichlorophenol | 1000 | 1500 | 620 | 2000 | 500 | 500 | ---- | ---- | ---- |
| **Inorganic components** | | | | | | | | | |
| Chlorine | 11400 | 12600 | 14100 | 19400 | 18900 | 14000 | ---- | ---- | ---- |
| Arsenic | 9.0 | 9.9 | 10.6 | 8.1 | 10.6 | 10.9 | ---- | ---- | ---- |
| Cadmium | 1.4 | 1.9 | 2.0 | 2.8 | 1.5 | 1.7 | ---- | ---- | ---- |
| Chromium | 7.9 | 7.5 | 7.2 | 12.3 | 7.8 | 7.9 | ---- | ---- | ---- |
| Lead | 1370 | 1350 | 1440 | 1220 | 1470 | 1490 | ---- | ---- | ---- |
| Zinc | 668 | 620 | 643 | 601 | 733 | 740 | ---- | ---- | ---- |

## TABLE 3. WASTE OIL INCINERATION TESTS: SITE F

| Organic components | Results of flue gas analysis (µg/M$^3$) 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| **Volatiles** | | | | | | | | | |
| Chloroform | ---- | ---- | ---- | 82.5 | ND[a] | 70.1 | 278 | 60 | 30[a] |
| Trichloroethane | ---- | ---- | ---- | 47.5 | 81.4 | 777 | 700 | 460 | 375 |
| Trichloroethylene | ---- | ---- | ---- | 86.7 | 72.3 | 171 | ---- | ---- | ---- |
| Tetrachloroethylene | ---- | ---- | ---- | 79.4 | 75.4 | 157 | 283 | 210 | 185 |
| **Semi-Volatiles** | | | | | | | | | |
| 2-Chlorophenol[b] | ---- | ---- | ---- | 20 | 4 | ---- | ---- | ---- | ---- |
| Tetrachlorobenzene[b] | ---- | ---- | ---- | 20 | 4 | ---- | ---- | ---- | ---- |
| Trichlorobenzene[b] | 11.6 | ND | ---- | 94.1 | 40.1 | 85.6 | ---- | ---- | ---- |
| 1-chloronaphthalene[b] | 9.4 | ND | ---- | 57.1 | 34.6 | 73.4 | ---- | ---- | ---- |
| Trichlorophenol[b] | ND | ND | ---- | ND | ND | ND | ---- | ---- | ---- |
| Phenol[b] | ---- | 22 | ---- | 21 | 32 | 20 | ---- | ---- | ---- |
| Phenanthrene | ---- | ---- | ---- | 14 | 18 | 23 | ---- | ---- | ---- |
| 1,2 Dichlorobenzene[b] | ---- | ---- | ---- | 33 | 37 | 20 | ---- | ---- | ---- |
| 1,3/1,4-Dichlorobenzene[b] | ---- | ---- | ---- | 18 | ---- | 10 | ---- | ---- | ---- |
| Benzene, chloromethyl | ---- | 13 | ---- | ---- | 12 | ---- | ---- | ---- | ---- |
| Napthalene[b,c] | 21 | 8 | ---- | 46 | 42 | 43 | ---- | ---- | ---- |
| Benzene, dimethyl, isomers[c] | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Benzene, alkyl $C_8H_{10}$ isomers[c] | ---- | ---- | ---- | 11 | ---- | 26 | ---- | ---- | ---- |
| Benzene, alkyl $C_9H_{12}$ isomers[c] | ---- | ---- | ---- | 11 | ---- | 64 | ---- | ---- | ---- |
| Benzene, alkyl, $C_{10}H_{14}$ isomers[c] | ---- | 8.5 | ---- | ---- | ---- | 99 | ---- | ---- | ---- |
| Benzaldehyde, alkyl isomers[c] | 51 | ---- | ---- | ---- | 19 | 44 | ---- | ---- | ---- |
| Benzoic acid[c] | 348 | 271 | ---- | 271 | 195 | 397 | ---- | ---- | ---- |
| Napthalene, methyl isomers[c] | 16 | ---- | ---- | ---- | 25 | 20 | ---- | ---- | ---- |
| **Inorganic components** | | | | | | | | | |
| **ICAP Analysis** | | | | | | | | | |
| Arsenic | ---- | ---- | 251 | ---- | ---- | ---- | ---- | ---- | ---- |
| Cadmium | ---- | ---- | 350 | ---- | ---- | ---- | ---- | ---- | ---- |
| Chromium | ---- | ---- | 205 | ---- | ---- | ---- | ---- | ---- | ---- |
| Lead | ---- | ---- | 49800 | ---- | ---- | ---- | ---- | ---- | ---- |
| Zinc | ---- | ---- | 26800 | ---- | ---- | ---- | ---- | ---- | ---- |
| **Ion Chromatograph Analysis** | | | | | | | | | |
| HCl | ---- | ---- | 430000 | ---- | ---- | ---- | ---- | ---- | ---- |

ND = <6 µg/m$^3$

[a] Trace amount quantified to one significant digit.

[b] Appendix VIII compound.

[c] Component is a known contaminant of XAD resin and/or may be formed during the exposure of resin to combustion source flue gases.

TABLE 4. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS: SITE F

| Component | µg/m³ |  |  |  |  | Detection Limit (ND = ) |
|---|---|---|---|---|---|---|
|  | Run |  |  |  |  |  |
|  | 1 | 2 | 3 | 4 | 6 |  |
| dibenzofuran | ND | ND | 20 | 7.4 | 21 | 0.08 |
| chlorodibenzofurans | ND | ND | 2.1 | ND | ND | 0.05 |
| dichlorodibenzofurans | ND | ND | ND | ND | ND | 0.08 |
| trichlorodibenzofurans | ND | ND | ND | ND | ND | 0.08 |
| tetrachlorodibenzofurans | ND | ND | ND | ND | ND | 0.10 |
| pentachlorodibenzofurans | ND | ND | ND | ND | ND | 0.22 |
| hexachlorodibenzofurans | ND | ND | ND | ND | ND | 0.22 |
| heptachlorodibenzofurans | ND | ND | ND | ND | ND | 0.60 |
| octachlorodibenzofurans | ND | ND | ND | ND | ND | 3.0 |
| dibenzodioxin | ND | ND | ND | ND | ND | 0.08 |
| chlorodibenzodioxins | ND | ND | ND | ND | ND | 0.05 |
| dichlorodibenzodioxins | ND | ND | ND | 2.4 | ND | 0.08 |
| trichlorodibenzodioxins | ND | ND | ND | ND | ND | 0.08 |
| tetrachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.10 |
| pentachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.22 |
| hexachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.22 |
| heptachlorodibenzodioxins | ND | ND | ND | ND | ND | 0.60 |
| octachlorodibenzodioxins | ND | ND | 17 | ND | ND | 3.0 |

## TABLE 5. WASTE OIL INCINERATION TESTS: SITE F

| Organic components | Destruction and removal efficiencies (percent)<br>1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| **Volatile Components** | | | | | | | | | |
| Chloroform | ---- | ---- | ---- | 99.95 | 99.99 | 99.96 | 99.90 | 99.93 | 99.92 |
| Trichloroethane | ---- | ---- | ---- | 99.98 | 99.96 | 99.58 | 99.86 | 99.76 | 99.68 |
| Trichloroethylene | ---- | ---- | ---- | 99.94 | 99.96 | 99.87 | ND | ND | ND |
| Tetrachloroethylene | ---- | ---- | ---- | 99.98 | 99.97 | 99.96 | 99.93 | 99.76 | 99.51 |
| **Semi-Volatiles** | | | | | | | | | |
| Trichlorobenzene | 99.99 | >99.99 | ---- | 99.93 | 99.97 | 99.92 | ---- | ---- | ---- |
| 1-chloronaphthalene | 99.99 | >99.99 | ---- | 99.98 | 99.98 | 99.94 | ---- | ---- | ---- |
| Trichlorophenol | >99.99 | >99.99 | ---- | >99.99 | >99.98 | >99.97 | ---- | ---- | ---- |

Site: G

Service: Heat and Process Steam for a Greenhouse Complex

Boiler Type: Cleaver Brooks, Four Pass Scotch Firetube

Rated Capacity ($10^6$ Btu/hr): 12.5

Atomization Method: Air

Stack Height (ft): 30

Stack Diameter (ft): 1.8

TABLE 1. WASTE OIL INCINERATION TESTS: SITE G - FLUE GAS DATA

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Fuel feed (gal/hr) | 26.18 | 27.43 | 22.32 | 16.54 |
| Stack T (°F) | 208 | 214 | 194.6 | 194 |
| Volumetric flow rate (dscm/hr) | 1668.6 | 1647.7 | 1707.3 | 1584.6 |
| Moisture content (percent) | 10.1 | 10.9 | 9.4 | 17.3 |
| $O_2$ (percent) | 7.2 | 6.9 | 7.3 | 6.8 |
| $CO_2$ (percent) | 9.5 | 10.0 | 8.2 | 8.3 |
| CO (ppm) | 50 | 50 | 50 | 40 |
| Excess Air | 49 | 46 | 49 | 44 |
| Particulate collected (mg) | 221.1 | 180.5 | 226.0 | 234.0 |
| Particulate emissions (lb/hr) | 1.2 | 0.98 | 1.2 | 1.1 |

TABLE 2. WASTE OIL INCINERATION TESTS: SITE G

| | Results of oil analysis (µg/g) | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Volatiles | | | | |
| Chloroform | 5000 | 2000 | 5000 | 10,000 |
| Trichloroethane | 5300 | 2500 | 5700 | -- |
| Trichloroethylene | 3700 | 1800 | 3400 | -- |
| Tetrachloroethylene | 7000 | 2600 | 5700 | 7600 |
| Semivolatiles | | | | |
| Trichlorobenzene | 2200 | 1600 | 1700 | 2800 |
| 1-chloronaphthalene | 2400 | 1400 | 3100 | -- |
| Chlorotoluene | NA | NA | NA | |
| Inorganic components | | | | |
| Chlorine | 12000 | 8200 | 12300 | NA |
| Arsenic | 9.2 | NA | 8.9 | NA |
| Cadmium | 2.0 | NA | 2.1 | NA |
| Chromium | 6.8 | NA | 7.6 | NA |
| Lead | 1580 | NA | 1510 | NA |
| Zinc | 775 | NA | 744 | NA |

NA = Results not available.

TABLE 3. WASTE OIL INCINERATION TESTS: SITE G

| Organic components | Results of flue gas analysis ($\mu g/m^3$) 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Volatiles | | | | |
| Chloroform | 60 | 100 | 100 | 155 |
| Trichloroethane | 69 | 115 | 230 | -- |
| Trichloroethylene | 95 | 150 | 290 | -- |
| Tetrachloroethylene | 75 | 60[a] | 160 | 120 |
| Semivolatiles | | | | |
| Trichlorobenzene | -- | 28 | 210 | 29 |
| 1-chloronaphthalene | -- | 58 | 120 | -- |
| Chlorotoluene | -- | 75 | 280 | -- |
| Naphthalene[b,c] | | 47 | 50 | |
| Naphthalene, methyl isomers[c] | | 270 | 130 | 35 |
| Naphthalene, dimethyl/ehtyl isomers[c] | | | 120 | 29 |
| Benzaldehyde[c] | | | | 16 |
| Benzaldehyde, methyl isomers[c] | | | | 32 |
| Benzene, alkyl, $C_9H_{12}$ isomers[c] | | | 330 | |
| Benzene, alkyl, $C_{10}H_{12}$ isomers[c] | | | 1000 | |
| Benzoic acid[c] | | | | 87 |
| Pentadecanoic acid | | | | 10 |
| Inorganic components | | | | |
| ICAP Analysis | | | | |
| Arsenic | 286 | | | |
| Cadmium | 81 | | | |
| Chromium | 263 | | | |
| Lead | 51000 | | | |
| Zinc | 27000 | | | |
| Ion Chromatograph Analysis | | | | |
| HCl | 903,000 | | | |

ND = < 9.0 $\mu g/m^3$.

[a] Trace amount quantified to one significant digit.

[b] Appendix VIII Compound.

[c] Component is a known contaminant of XAD resin and/or may be formed during the exposure of resin to combustion source flue gases.

TABLE 4. ANALYSIS FOR CHLORINATED DIBENZOFURANS AND DIBENZODIOXINS: SITE G

| Component | µg/m³ | | | | Detection Limit (ND = ) |
|---|---|---|---|---|---|
| | Run | | | | |
| | 1 | 2 | 3 | 4 | |
| dibenzofuran | 2.1 | 3.7 | 2.2 | ND | 0.07 |
| chlorodibenzofurans | ND | ND | ND | ND | 0.04 |
| dichlorodibenzofurans | ND | ND | ND | ND | 0.07 |
| trichlorodibenzofurans | ND | ND | ND | ND | 0.07 |
| tetrachlorodibenzofurans | ND | ND | ND | ND | 0.08 |
| pentachlorodibenzofurans | ND | ND | ND | ND | 0.21 |
| hexachlorodibenzofurans | ND | ND | ND | ND | 0.21 |
| heptachlorodibenzofurans | ND | ND | ND | ND | 0.60 |
| octachlorodibenzofurans | ND | ND | ND | ND | 3.0 |
| dibenzodioxin | ND | ND | ND | ND | 0.07 |
| chlorodibenzodioxins | ND | ND | ND | ND | 0.04 |
| dichlorodibenzodioxins | ND | ND | ND | ND | 0.07 |
| trichlorodibenzodioxins | ND | ND | ND | ND | 0.07 |
| tetrachlorodibenzodioxins | ND | ND | 1.4 | ND | 0.08 |
| pentachlorodibenzodioxins | ND | ND | ND | ND | 0.21 |
| hexachlorodibenzodioxins | ND | ND | ND | ND | 0.21 |
| heptachlorodibenzodioxins | ND | ND | ND | ND | 0.60 |
| octachlorodibenzodioxins | ND | ND | ND | ND | 3.0 |

TABLE 5. WASTE OIL INCINERATION TESTS: SITE G

| | Destruction and removal efficiences (percent) | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Volatile components | | | | |
| Chloroform | 99.98 | 99.91 | 99.95 | 99.96 |
| Trichloroethane | 99.97 | 99.92 | 99.91 | -- |
| Trichloroethylene | 99.95 | 99.85 | 99.81 | -- |
| Tetrachloroethylene | 99.98 | 99.96 | 99.94 | 99.95 |
| Semivolatiles | | | | |
| Trichlorobenzene | -- | 99.97 | 99.72 | 99.97 |
| 1-chloronaphthalene | -- | 99.93 | 99.91 | -- |

# APPENDIX B

## SAMPLE CALCULATIONS

- According to 40 CFR Part 264, the DRE for each POHC is calculated as:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100\%$$

Where:

$W_{in}$ = mass feed rate of one POHC in the waste stream feeding the incinerator, and

$W_{out}$ = mass emission rate of the same POHC present in stack exhaust emissions.

a. Calculations of $W_{in}$ (lb/hr)

$$W_{in} = \frac{C_w \times FR_w}{100}$$

Where:

$C_w$ = Concentration one POHC in the waste, %

$FR_w$ = **Mass Feed Rate of waste to the incinerator, lb/hr.**

- **The stack emission rate of HCl can be calculated from:**

$$HCl_{out} = C_{in} \times ER_s \times 1.32 \times 10^{-4}$$

Where: $C_{in}$ = concentration of HCl (as $Cl^-$) in the stack gas effluent and collected in the impingers

$ER_s$ = volumetric flow rate of the stack gas in $m^3$/min.

**$1.32 \times 10^{-4}$ = conversion factor from mg/min to lb/hr.**

Facility______________________
Source______________________
Run______________________

Job No.______________________
Date______________________
Calc/Review______________________

## SAMPLE CALCULATIONS

Particulate Isokinetic Sampling

I. Calculations for stack volume and Isokinetic Ratio

| Time | Dry Gas Meter ft$^3$ | Pitot $\Delta P$, in. $H_2O$ | Orifice $\Delta H$, in. $H_2O$ | Dry Gas Temp °F In Out | Stack Static Pressure in. $H_2O$ | Stack Temp °F |
|---|---|---|---|---|---|---|
| T | VM | $\Delta P$ | PM | TMI TMO | PST | TS |

1. DN - Nozzle Diameter, inches ______________ in.
2. PB = Barometric Pressure, inches Hg ______________ in. Hg
3. TT = Net Sampling Time, minutes ______________ min.
4. VM = VM final - VM initial = Sample Gas Volume, ft$^3$ ______________ ft$^3$

4A. VML = Use only if any final or intermediate leak check rate is over 0.02 cfm

LI = Leak rate after any given sampling period, cfm

TLI = Total time of sampling period in which leak occurred, min.

VML = VM - [(L1 - 0.02) TL1 + (L2 - 0.02) TL2 + (L3 - 0.02) TL3 + L4 + 0.02) TL4]

= (          ) - [(          - 0.02)(          )+(          - 0.02)(          )+(          - 0.02)
(          )+(          - 0.02)(          )]

= (          ) - [(          )+(          )+(          )+(          )]

= (          ) - (          ) = ______________ ft$^3$

5. TM = Average Dry Gas Temperature at Meter, °F

$$TM = \frac{\text{Avg. TMI} + \text{Avg. TMO}}{2}$$

= ______________ °F

6. PM = Average Orifice Pressure Drop, inches $H_2O$

PM = Avg. $\Delta$ H = ______ ÷ 13.6 = ______ in.Hg

7. Volume of dry gas sampled at standard conditions,[a] dscf

$$VMSTD = \frac{528\ (Y)(VM)\left(PB + \frac{PM}{13.6}\right)}{29.92\ (TM + 460)}$$

Y = dry gas meter calibration factor ______________

$$= \frac{528\ (\qquad)(\qquad)(\qquad)}{29.92\ (\qquad)} = \underline{\qquad\qquad}\ ft^3$$

Job No.__________________________
Run No.__________________________

8. VW = Total Water Collected = gm $H_2O$ Silica gel + ml Imp. $H_2O$ = ml

( ) + ( ) = __________

9. Volume of water vapor at standard conditions, scf

VW gas = 0.04715 × VW = scf = 0.04715 ( ) = __________ $ft^3$

10. Percent moisture in stack gas

$$\% M = \frac{100 \times VW\ gas}{VMSTD + VW\ gas} = \frac{100\ (\qquad)}{(\qquad) + (\qquad)} = \frac{(\qquad)}{(\qquad)} =$$

= __________%

11. Mole fraction of dry gas

$$MD = \frac{100 - \%M}{100} = \frac{100 - (\qquad)}{100} = \underline{\qquad\qquad}$$

12. Molecular weight of dry stack gas

$$MWD = (\%CO_2 \times \frac{44}{100}) + (\%O_2 \times \frac{32}{100} + \left[(\%CO + \%N_2) \times \frac{28}{100}\right]$$

$$= (\qquad \times 0.44) + (\qquad \times 0.32) + (\qquad \times 0.28)$$

$$= (\qquad) + (\qquad) + (\qquad) = \underline{\qquad}\ lb/lb\ mole\ dry$$

12A. $\%EA = \%\ Excess\ Air = \frac{[(\%\ O_2 - 0.5\ (\%CO)] \times 100}{[(0.264(\%N_2)] - (\%\ O_2) + 0.5\%\ (CO)}$

$$= \frac{(\qquad - \qquad) \times 100}{[(0.264\ (\qquad)] - (\qquad) + 0.5\ (\qquad)}$$

$$= \frac{(\qquad) \times 100}{(\qquad) - (\qquad) + (\qquad)} = \underline{\qquad}\%$$

13. Molecular weight of wet stack gas

MW = MWD × MD + 18 (1 - MD)

= ( ) ( ) + 18(1 - )

= ( ) + ( ) = __________ lb/lb mole wet

14. AS = Stack Area, square inches

$$\text{Circular, } = \left(\frac{\text{Stack diameter}}{2}\right)^2 \pi = \left(\frac{\qquad}{2}\right)^2 \pi = \underline{\qquad\qquad}\ \text{sg. in.}$$

Rectangular, = Length × width=( )( ) = __________ sq. in.

15. PS = Stack Pressure, absolute, inches Hg = PB ± AV PST

PST = Stack static pressure

Job No.____________________
Run No.____________________

$$\text{PST in. Hg} = \frac{\text{PST in. H}_2\text{O}}{13.6} = \frac{\qquad}{13.6} = \underline{\qquad\quad}\text{ in. Hg}$$

$$\text{PS} = \text{PB} \pm \text{Avg. PST} = (\qquad)\,(\qquad) = \underline{\qquad\qquad}\text{ in. Hg}$$

16. TS = Average Stack Temperature, $\underline{\qquad}\,^{\circ}\text{F} + 460 = \underline{\qquad}\,^{\circ}\text{R}$

$$\text{TS} = \text{Average TS} \qquad \sqrt{\text{TS}_{\text{AV}} + 460} = \underline{\qquad\qquad}$$

17. $\text{SDE}_{\text{AV}} = (\sqrt{\Delta P})_{\text{AV}} \times \sqrt{\text{TS}_{\text{AV}} + 460)} = (\qquad)\,(\qquad) = \underline{\qquad\qquad}$

18. Stack gas velocity at stack conditions, afpm

$$\text{VS} = 5130^{(e)} \times \text{Cp} \times \text{Avg. (SDE)} \times \left[\frac{1}{\text{PS} \times \text{MW}}\right]^{\frac{1}{2}} = \text{afpm} \qquad \text{Cp} = \text{pitot tube coefficient}$$

$$= 5130 \times (\qquad) \times (\qquad) \times \left[\frac{1}{(\qquad)(\qquad)}\right]^{\frac{1}{2}} = \underline{\qquad\qquad\qquad}\text{afpm}$$

19. Stack gas volumetric flow rate at standard conditions,[c] dscfm

$$Q_s = \frac{528 \times \text{VS} \times \text{AS} \times \text{MD} \times \text{PS}}{(29.92)(144)(\text{TS} + 460)} = \text{dscfm}$$

$$= \frac{528\ (\qquad) \times (\qquad) \times (\qquad) \times (\qquad)}{29.92 \times 144\ (\qquad)} = \underline{\qquad\qquad}\text{dscfm}$$

20. Stack gas volumetric flow rate at stack conditions, acfm[d]

$$Q_a = \frac{29.92 \times \text{QS}\ (\text{TS} + 460)}{(528)\ (\text{PS})\ (\text{MD})} = \text{acfm}$$

$$= \frac{29.92\ (\qquad)(\qquad)}{528\ \ (\qquad)(\qquad)} = \underline{\qquad\qquad}\text{acfm}$$

21. Percent isokinetics

$$\%\ \text{I} = \frac{1{,}039^{(f)} \times (\text{TS} + 460) \times \text{VMSTD}}{\text{VS} \times \text{TT} \times \text{PS} \times \text{MD} \times (\text{DN})^2}$$

---

[a] Dry standard cubic feet at 68°F (528R) and 29.92 in. Hg.

[b] Standard conditions at 68°F (528R) and 29.92 in. Hg.

[c] Dry standard cubic feet per minute at 68°F (528) and 29.92 in. Hg.

[d] Actual cubic feet per minute

[e] $5130 = 85.5\ \frac{\text{ft}}{\text{sec}} \left[\frac{(\text{lb/lb mole})(\text{in. Hg})}{(^{\circ}\text{R})(\text{in. H}_2\text{O})}\right]^{\frac{1}{2}} \times 60\ \text{sec/min}$

[f] $1039 = \frac{29.92\ \text{in. Hg}}{528\ \text{DegR}} \times \frac{144\ \text{in.}^2}{\text{ft}^2} \times \frac{4}{\pi} \times 100$

Job No.________________________
Run No.________________________

$$= \frac{1{,}039 \times (\qquad) \times (\qquad)}{(\qquad) \times (\qquad) \times (\qquad) \times (\qquad) \times (\qquad)^2}$$

$= \underline{\qquad\qquad}\%$

II. Calculations for grain loading and emission rates

22. Particulate, gr/dscf

$$\text{gr/dscf} = 0.0154 \times \frac{\text{mg}}{\text{VMSTD}} = \frac{0.0154\ (\qquad)}{(\qquad)} = \underline{\qquad\qquad}\text{gr/dscf}$$

23. Particulate at stack conditions, gr/acf

$$\text{gr/acf} = \frac{528 \times \text{gr/dscf} \times \text{PS} \times \text{MD}}{29.92\ (\text{TS} + 460)}$$

$$= \frac{528\ (\qquad) \times (\qquad) \times (\qquad)}{29.92\ (\qquad)} = \underline{\qquad\qquad}\text{gr/acf}$$

24. Particulate, lb/hr conc. method

$$\text{lb/hr} = \frac{60\ \text{min/hr} \times \text{gr/dscf} \times \text{QS}}{7000\ \text{gr/lb}} = \frac{60\ \text{min/hr}}{7000\ \text{gr/lb}} \times (\qquad\qquad) \times (\qquad\qquad)$$

$= \underline{\qquad\qquad}\text{lb/hr}$

25. Particulate lb/hr area method $= 0.132 \times \dfrac{\text{gms particulate} \times \text{AS}}{\pi\left(\dfrac{\text{DN}}{2}\right)^2 \times \text{TT}}$

$$= \frac{0.132 \times (\qquad) \times (\qquad)}{\pi\left(\frac{\qquad}{2}\right)^2 \times (\qquad)} = \underline{\qquad\qquad\qquad} = \underline{\qquad\qquad}\text{lb/hr}$$

26. $\dfrac{\text{lb/hr area} \times 100}{\text{lb/hr conc.}} = \dfrac{(\qquad)}{(\qquad)} \times 100 = \underline{\qquad\qquad}\%\ \text{I}$

27. Particulate combustion lb/$10^6$ Btu heat input method

lb/hr = avg. of area and conc. method = ________________

$10^6$ Btu from fuel flow, steam generation or heat rate = ________________

$$\frac{\text{lb/hr}}{10^6\ \text{Btu hr}} = \frac{(\qquad)}{(\qquad)} = \underline{\qquad\qquad}\text{lb}/10^6\ \text{Btu}$$

28. lb/$10^6$ Btu F Factor method =

$$\frac{\text{gr/dscf}}{7000} \times \text{F} \times \frac{20.9}{(20.9 - \%\ \text{O}_2)} = \frac{\qquad}{7000} \times (\qquad) \times \frac{20.9}{[20.9 - (\qquad)]}$$

$$= \frac{\qquad}{7000} \times (\qquad) \times \frac{(20.9)}{(\qquad)} =$$

$= \underline{\qquad\qquad}\text{lb}/10^6\ \text{Btu}$

Job No.__________________________

Run No.__________________________

29. Density of stack gas

a. Wet at stack condition = MW lb/lb mol $\Big/ \left[21.85 \times \left(\frac{TS + 460}{PS}\right)\right]$

$= (\quad\quad) \Big/ \left[21.85 \times \frac{(\quad\quad)}{(\quad\quad)}\right] = (\quad\quad) \Big/ (\quad\quad) =$ _____lb/lb mole wet

b. Dry at 68°F (528R) and 29.92 in. Hg = MWD/385.6

= (        )/385.6 = __________lb/lb mole dry

30. Exhaust gas flow rate

a. lb/hr dry = QS × 60 × density dry

FRS = (        ) × 60 × (        ) = __________lb/hr

b. lb/hr wet = QA × 60 × density wet

FRA = (        ) × 60 × (        ) = __________lb/hr

31. gr/dscf at 12% $CO_2$ = gr/dscf × $\frac{12}{\%\ CO_2}$

$= (\quad\quad) \times \frac{12}{(\quad\quad)} =$ __________gr/dscf

32. gr/dscf at 50% excess air = $\frac{100 + EA}{150}$ × gr/dscf

$= \frac{(\quad\quad) + 100}{150} \times (\quad\quad) =$ _________gr/dscf

33. lb pollutant/1000 lb flue gas at 12% $CO_2$

wet or dry $= \frac{\text{lb pollutant/hr}}{\text{FRA or FRS}} \times \frac{12}{\%\ CO_2} \times 1000$

$= \frac{(\quad\quad)}{(\quad\quad)} \frac{12}{(\quad\quad)} \times 1000$

= __________lb/1000 lb

# APPENDIX C

# CALIBRATIONS

Date September 30, 1982 Box No. 2547

Barometric pressure, $P_b$ = 30.3 in. Hg Dry gas meter No. —

| Orifice manometer setting, $\Delta H$, in. $H_2O$ | Gas volume wet test meter $V_w$, $ft^3$ | Gas volume dry gas meter $V_d$, $ft^3$ | Temperature: Wet test: Meter $t_w$, °F | Temperature: Dry gas meter: Inlet $t_{di}$, °F | Temperature: Dry gas meter: Outlet $t_{do}$, °F | Temperature: Dry gas meter: Average $t_d$, °F | Time θ, min | γ | $\Delta H_@$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 5 | 5.054 | 63.5 | | | 76.25 | 12.94 | 1.01 | 1.791 | 1.012 | ✓ |
| 1.0 | 5 | 5.037 | 63.5 | | | 75.50 | 9.16 | 1.01 | 1.797 | 1.012 | ✓ |
| 2.0 | ~~10~~ 5 | 5.152 | 63.5 | | | 83.0 | 6.34 | 1.00 | 1.698 | ✓ | ✓ |
| 1.5 ~~4.0~~ | ~~10~~ 5 | 5.152 | 63.5 | | | 8.20 | 7.39 | 1.00 | 1.733 | ✓ | ✓ |
| 6.0 | 10 | | | | | | | | | | |
| 8.0 | 10 | | | | | | | | | | |
| | | | | | | Average | | 1.002 | 1.754 | | |

Calculations

| $\Delta H$ | $\frac{\Delta H}{13.6}$ | γ: $\frac{V_w P_b (t_d + 460)}{V_d\left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 460)}$ | $\Delta H_@$: $\frac{0.0317\ \Delta H}{P_b\ (t_d + 460)}\left[\frac{(t_w + 460)\ \theta}{V_w}\right]^2$ |
|---|---|---|---|
| 0.5 | 0.0368 | | |
| 1.0 | 0.0737 | | |
| 2.0 | 0.147 | | |
| 4.0 | 0.294 | | |
| 6.0 | 0.431 | | |
| 8.0 | 0.588 | | |

γ = Ratio of accuracy of wet test meter to dry test meter. Tolerance = ± 0.01

$\Delta H_@$ = Orifice pressure differential that gives 0.75 cfm of air at 70° F and 29.92 inches of mercury, in. $H_2O$. Tolerance - ± 0.15

Ckd 10/7
MW

Calibrated By A WILDER

Barometric Pressure, Pb= 29.68 in.Hg

Date 11 MAR 83

Dry Gas Meter No. ______

Control Box No. 2282

| Orifice manometer setting, ΔH, in. $H_2O$ | Gas volume wet test meter $V_w$, $ft^3$ | Gas volume dry gas meter $V_d$, $ft^3$ | Temperature | | | | Time θ, min | Y | ΔH@ | Deviation | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Wet test | Dry gas meter | | | | | | | |
| | | | Meter $t_w$, °F | Inlet $t_{di}$, °F | Outlet $t_{do}$, °F | Average $t_d$, °F | | | | Y | ΔH@ |
| 0.5 | ~~8~~6 | 5.991 | 63 | 63 | 79 | 71 | 14.98 | 1.015 | 1.715 | | |
| 1.0 | 5 | 5.203 | 63 | 73 | 93 | 83 | 9.13 | .995 | 1.794 | | |
| 2.0 | 10 | 10.276 | 63 | 78 | 95 | 86.5 | 13.35 | 1.011 | 1.905 | | |
| | | | | | | | Average | 1.007 | 1.805 | | |

Calculations

| Y | ΔH@ |
|---|---|
| $\dfrac{V_w P_b (t_d + 460)}{V_d\left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 460)}$ | $\dfrac{0.0317\ \Delta H}{P_b\ (t_d + 460)}\left[\dfrac{(t_w + 460)\ \theta}{V_w}\right]^2$ |

Y = Ratio of accuracy of wet test meter to dry test meter. Tolerance = ± 0.01

ΔH@ = Orifice pressure differential that gives 0.75 cfm of air at 70° F and 29.92 inches of mercury, in. $H_2O$. Tolerance - ± 0.15

Fine Adj KNOB needs to be loosened

Maintenance Checklist

Vacuum System: Oil Reservoir Level ✓; Knockout Jar ✓.
Vacuum Gage ✓; Leak Chk (No Leak) 15" Hg ✓
Quick Connects: Clean ✓ Lubricate ✓
Manometer: Check for Leaks ✓; Fluid Level ✓; Clean Surface ✓
Solenoid Valve: Check for Click ✓
Fuses: 2.5 amp. Probe Heater ✓; 7 amp. Pump ✓; 10 amp. Heater ✓
Amphenol Connector ______(Check with umbilical cord connected to hot box)
Variable XFormer ______(Check Operation with Probe or Light)

(All Items Must Be Checked and Initialed)

Calibrated By M White

Barometric Pressure, Pb= 30.10 in.Hg

Date 5/7/82

Dry Gas Meter No. _____

Control Box No. 2180

| Orifice manometer setting, ΔH, in. $H_2O$ | Gas volume wet test meter $V_w$, $ft^3$ | Gas volume dry gas meter $V_d$, $ft^3$ | Temperature | | | | Time θ, min | γ | ΔH@ | Deviation | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Wet test | Dry gas meter | | | | | | | |
| | | | Meter $t_w$, °F | Inlet $t_{di}$, °F | Outlet $t_{do}$, °F | Average $t_d$, °F | | | | γ | ΔH@ |
| 0.5 | 5 | 5.196 | 73 | 108 | 88 | 98 | 12.92 | 0.999 | 1.802 | 0.001 | 0.071 |
| 1.0 | 5 | 5.707 | 73 | 101 | 85 | 93 | 10.31 | 0.997 | 1.901 | 0.001 | 0.028 |
| 2.0 | 10 | 10.431 | 73 | 108 | 88 | 98 | 13.37 | 0.999 | 1.917 | 0.001 | 0.044 |
| | | | | | | | Average | 0.998 | 1.873 | | |

Calculations

| γ | ΔH@ |
|---|---|
| $\dfrac{V_w P_b (t_d + 460)}{V_d\left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 460)}$ | $\dfrac{0.0317\ \Delta H}{P_b\ (t_d + 460)}\left[\dfrac{(t_w + 460)\ \theta}{V_w}\right]^2$ |

γ = Ratio of accuracy of wet test meter to dry test meter. Tolerance = ± 0.01

ΔH@ = Orifice pressure differential that gives 0.75 cfm of air at 70° F and 29.92 inches of mercury, in. $H_2O$. Tolerance - ± 0.15

Maintenance Checklist

Vacuum System: Oil Reservoir Level ✓; Knockout Jar ✓.
Vacuum Gage ✓; Leak Chk (No Leak) 15" Hg ✓
Quick Connects: Clean ✓ Lubricate ✓
Manometer: Check for Leaks ✓; Fluid Level ✓; Clean Surface ✓
Solenoid Valve: Check for Click ✓
Fuses: 2.5 amp. Probe Heater ✓; 7 amp. Pump ✓; 10 amp. Heater ✓
Amphenol Connector _____(Check with umbilical cord connected to hot box)
Variable XFormer _____(Check Operation with Probe or Light)

(All Items Must Be Checked and Initialed)

Date 10-1-82

Box No. 1725 ~~[illegible]~~

Barometric pressure, $P_b$ 29.91 in. Hg

Dry gas meter No. ____

| Orifice manometer setting, ΔH, in. $H_2O$ | Gas volume wet test meter $V_w$, $ft^3$ | Gas volume dry gas meter $V_d$, $ft^3$ | Temperature | | | | Time θ, min | γ | ΔH@ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Wet test | Dry gas meter | | | | | | |
| | | | Meter $t_w$, °F | Inlet $t_{di}$, °F | Outlet $t_{do}$, °F | Average $t_d$, °F | | | | |
| 0.5 | 5 | 4.991 | 66 | | | 77.25 | 13.41 | 1.02 | 1.94 | 1.96 |
| 1.0 | 5 | 5.015 | 66 | | | 80.6 | 9.46 | 1.01 | 1.92 | 1.022 1.94 |
| 2.0 | 10 | 10.088 | 66 | | | 88 | 13.64 | 1.01 | 1.871 | 1.027 1.99 |
| 1.5 ~~4.0~~ | 10 | 10.159 | 66 | | | 81.25 | 15.25 | 1.02 | 1.98 | 1.001 1.89 |
| 6.0 | 10 | | | | | | | | | |
| 8.0 | 10 | | | | | | | | | |
| | | | | | | Average | | 1.015 | 1.92 | 1.02 1.98 |

Calculations

| ΔH | $\frac{\Delta H}{13.6}$ | γ | ΔH@ |
|---|---|---|---|
| | | $\frac{V_w P_b (t_d + 460)}{V_d\left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 460)}$ | $\frac{0.0317\ \Delta H}{P_b\ (t_d + 460)}\left[\frac{(t_w + 460)\ \theta}{V_w}\right]^2$ |
| 0.5 | 0.0368 | | |
| 1.0 | 0.0737 | | |
| 2.0 | 0.147 | | |
| 4.0 | 0.294 | | |
| 6.0 | 0.431 | | |
| 8.0 | 0.588 | | |

γ = Ratio of accuracy of wet test meter to dry test meter. Tolerance = ± 0.01

ΔH@ = Orifice pressure differential that gives 0.75 cfm of air at 70° F and 29.92 inches of mercury, in. $H_2O$. Tolerance = ± 0.15

ck'd
10/7 MW

GCA
GCA CORPORATION
**Technology Division**
213 Burlington Road
Bedford, Massachusetts 01730
Telephone: 617-275-5444
Telex: 92-3339

SHEET 1 OF 1
BY M White
DATE 11/23/82
CH'K. BY R. [illegible]
DATE CH'K. 12/1/82
B'K. CH'K. BY

JOB NO. 1-619-068 and 1-452-126
PROJECT
SUBJECT DGM Calibrations for NuTech Boxes 6593 and 6633

$$\gamma = \frac{V_w * (T_D+460)}{V_D * (T_w+460)}$$

| | RATE | WTM | °F | DGM ° | °F | Time(min) | $\gamma$ |
|---|---|---|---|---|---|---|---|
| BOX DGM 6593 | Full/0.36 cfm | 47.00 | 64 | 839.696 | 70 | 13.70 | 1.008 |
| | | 42.00 | 64 | 834.687 | 68 | 0 | |
| | | 5.00 | | 5.009 | | $\frac{(5)(529)}{(5.009)(524)}$ | |
| | 2/3 / 0.31 cfm | 52.20 | 64 | 844.925 | 70 | 16.05 | 1.004 |
| | | 47.20 | 64 | 839.888 | 70 | 0 | |
| | | 5.00 | | 5.037 | | $\frac{(5)(530)}{(5.037)(524)}$ | |
| | 1 lpm/0.03 cfm | 53.40 | 64 | 846.130 | 70 | 34.5 | 1.003 |
| | | 52.25 | 64 | 844.970 | 70 | 0 | |
| | | 1.15 | | 1.160 | | $\frac{(1.15)(530)}{(1.16)(524)}$ | |
| | | | | | | | $\bar{\gamma}$ = 1.005 |
| DGM 6633 | Full/0.415 cfm | 69.5 | 65 | 797.232 | 74 | 16.84 | 0.996 |
| | | 62.5 | 65 | 790.112 | 70 | 0 | |
| | | 7.0 | | 7.120 | 72 | $\frac{(7)(532)}{(7.120)(525)}$ | |
| | 2/3/0.398 cfm | 75.3 | 65 | 803.166 | 74 | 12.55 | 0.993 |
| | | 70.3 | 65 | 798.043 | 74 | 0 | |
| | | 5.0 | | 5.123 | | $\frac{(5)(534)}{(5.123)(525)}$ | |
| | 1 lpm/0.033 cfm | 76.4 | 65 | 804.285 | 74 | 30.5 | 0.997 |
| | | 75.4 | 65 | 803.265 | 74 | 0 | |
| | | 1.0 | | 1.020 | | $\frac{(1.00)(534)}{(1.020)(525)}$ | |
| | | | | | | | $\bar{\gamma}$ = 0.995 |

GCA/TECHNOLOGY DIVISION

## THERMOCOUPLE CALIBRATION FORM

| Thermocouple Number | Temperature Reading 1 | Reference Temperature 1 | Temperature Reading 2 | Reference Temperature 2 | Temperature Reading 3 | Reference Temperature 3 |
|---|---|---|---|---|---|---|
| TC-17 | 69 | 68 | 210 | 212 | 32 | 32 |
| TC-17 | 69 | 68 | 212 | 212 | 32 | 32 |
| | | | | | | |
| TC-16 | 66 | 68 | 210 | 212 | 32 | 32 |
| TC-16 | 66 | 68 | 210 | 212 | 32 | 32 |
| | | | | | | |
| TC-15 | 66 | 68 | 211 | 212 | 32 | 32 |
| TC-15 | 67 | 68 | 211 | 212 | 32 | 32 |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Michael White

Signature of Person Performing Calibration

2/15/83

Calibration Date